PHYSICAL CHEMISTRY

TARGET CSIR NET

PREVIOUS YEAR SOLUTION'S

QUANTA
POINT

Address -"Quanta Chemistry Classes, 50 Mall Road, near GTB nagar
metro station, Gate no 3,
Kingsway Camp, GTB Nagar, New Delhi (110009) INDIA".
Tel.:9990382567, 9717373074, 8285815185
Email: Quantachemistryclasses@gmail.com
Website :www.quantachemistryclasses.com

QUANTA POINT

1

Solid State

Hints & Solutions

1. Correct answer is (b)

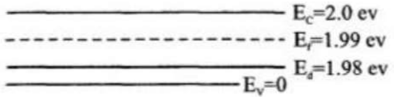
$$\text{width of conduction band} \propto \frac{1}{\text{lattice dimension}}$$

2. Correct answer is (b)

$$325.6 = \frac{\alpha}{\sqrt{1^2+1^2+1^2}} = \frac{\alpha}{\sqrt{3}}$$

$$\Rightarrow \alpha = 325.6 \times \sqrt{3} \qquad \Rightarrow \quad d_{333} = \frac{325.6\times\sqrt{3}}{\sqrt{3^2+3^1+3^2}} = \frac{325.6\times\sqrt{3}}{\sqrt{27}} = 108.5\text{pm}$$

3. Correct answer is (c)



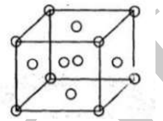
At T = 0 K,

$$E_f = \frac{E_c + E_d}{2} \quad , \quad E_f = \frac{2.0\text{eV} + 1.98\text{eV}}{2}$$

For fermi level lies exactly half any between the bottom or conduction band and the donor level. But as temperature is increased fermi level drops (i.e., Ef decreases).

4. Correct answer is (c)

Atoms that are packed in fcc structure. There are 8 atoms in the corner of a cube. Since a corner of cube is shared by 8 unit cells.



Hence total atoms contribution to a unit cell = 8 x 1/8= 1 atom.

Atom in a face is shared by two unit cells and there are 6 faces in the cube. Hence atoms = 6x1/2 = 3 atom. Total number of atoms in fcc = 3 + 1 = 4 atoms.

5. Correct answer is (c).

If the number of close packed spheres be N then the number of tetrahedral voids are 2N. Since all the tetrahedral holes are occupied. Hence the correct option is CaF_2

6. Correct answer is (b)

Given a = 4.04 Å

$$\text{For fcc lattice } r = \frac{a}{2\sqrt{2}} = \frac{4.04\,\text{Å}}{2\times1.44} = 1.428\,\text{Å}$$

QUANTA POINT

7. Correct answer is (b)

$$E = \frac{hc}{\lambda} \Rightarrow \lambda = \frac{hc}{E} = \frac{6.626\times10^{-34}\text{Jsec} \times 3 \times 10^{8}\text{ms}^{-1}}{1.98\times10^{-19}}$$

$= 10.039 \times10^{-7}\text{m} = 1003.9 \times 10^{-9}\text{ m} = 1003.9\text{ nm}$

This wavelength lies in the IR region

8. Correct answer is (all options are incorrect)

The angle between two planes having Miller Indices ($h_1\ k_1\ l_1$) & ($h_2\ k_2\ l_2$) is given by

$$\cos\theta = \frac{h_1h_2 + k_1k_2 + l_1l_2}{\sqrt{h_1^2 + k_1^2 + l_1^2}\sqrt{h_2^2 + k_2^2 + l_2^2}}$$

$$\cos\theta = \frac{1\times1 + 1\times1 + 0\times1}{\sqrt{1_1^2 + 1_1^2 + 0_1^2}\sqrt{1_2^2 + 1_2^2 + 1_2^2}} = \frac{2}{\sqrt{2}\sqrt{3}} = \frac{\sqrt{2}}{\sqrt{3}}$$

$\cos\theta = 0.816\,; \theta = \cos^{-1}(0.816)$

$\theta = 35.27°$

9. Correct answer is (c)

We have

$$\rho = \frac{ZM}{N_0a^3} \Rightarrow M = \frac{\rho N_0 a^3}{Z}$$

$$M = \frac{(1.33\text{g cm}^3)(6.023\times10^{23}mole^{-1})(500\times10^{-10}cm)^3}{4} = 25$$

10. Correct answer is (c)

$$\text{Packing fraction} = \frac{\text{volume occupied by particles}}{\text{total volume of the unit cell}}$$

$$= \frac{(\text{No. of particles per unit cell })\times(\text{volume of 1 particles})}{\text{total volume of the unit cell}}$$

For simple cubic lattice,

Number of particles per unit cell = 1

Volume of one particle= $4/3\ \pi r^3$

where, r = radius of one particle and a = unit cell edge length.

Then the total volume of the unit cell = a^3

$$Packing\ fraction = \frac{1\times\frac{4}{3}\pi r^3}{a^3} = \frac{4}{3}\times3.14 \times \frac{r^3}{(2r)^3} = 0.52$$

[for SCC, a=2r]

11. Correct answer is (a)

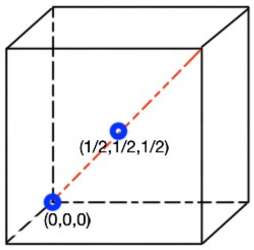
We know that, selection rule for allowed reflection for BCC and FCC lattice is

BCC h+k+l should be even

FCC h, k, l all either even or odd.

Therefore, A is FCC and B is BCC

12. Correct answer is (c)



$Z = 8 \times \frac{1}{8} + 1 \times 1 = 2$

Consider one particle at origin and second one at body center; (0, 0, 0) and (1/2, 1/2, 1/2)

13. Correct answer is (c)

$$d = \frac{a}{\sqrt{h^2 + l^2 + k^2}} = \frac{4}{\sqrt{1^2 + 0^2 + 0^2}} = 4$$

14. Correct answer is (c)

From Bragg's equation, 2d sin θ =n λ

2d sin θ = λ {for first order reflection n = 1}

$\Rightarrow d = \frac{\lambda}{2\sin\theta}$

Then for spacing 2d , we have

$2(2d)\sin\theta = \lambda \Rightarrow \sin\theta = \frac{\lambda}{4d} = \frac{\lambda}{4(\lambda/2\sin\theta)} = \frac{\sin\theta}{2}$

$$\theta = sin^{-1}\left(\frac{\sin\theta}{2}\right)$$

15. Correct answer is (c).

In case of Frenkel defect, ions are not missing from the lattice. They just displace into interstitial sites. Also, no extra ion come from outside into the lattice. Therefore, density remains same.

16. Correct answer is (d)

$M = 8 \times \frac{1}{8} + 1 \times 1 = 2$

$X = 6 \times \frac{1}{2} = 3$

Therefore, formula = M_2X_3

17. Correct answer is (a)

2d sin θ =n λ

$2\frac{a}{\sqrt{h^2+l^2+k^2}}\sin\theta = \lambda$ {for first order reflection n = 1}

$\sin\theta = \frac{\sqrt{h^2+l^2+k^2}}{2a} = \frac{2.29Å\sqrt{1^2+1^2+0^2}}{2\times3.28Å} = 0.5 = \frac{1}{2} = sin30°,\ \theta = 30°$

18. Correct answer is (a)

Since, K^+ and Cl^- are isoelectric, some of the peaks are missing entirely. The scattering intensities for X-rays are directly related to the number of electrons in the atom. Light atoms scatter X-rays weakly, while heavy atoms scatter X-rays more effectively.

19. Correct answer is (a)

$$\rho_{FCC} = \frac{ZM}{NV_{FCC}} = \frac{4M}{NV_{FCC}}$$

$$\rho_{BCC} = \frac{ZM}{NV_{BCC}} = \frac{4M}{NV_{FCC}} = \frac{2M}{NV_{BCC}}$$

$$\frac{(i)}{(ii)} \quad \frac{\rho_{FCC}}{\rho_{BCC}} = \frac{\frac{4M}{NV_{FCC}}}{\frac{2M}{NV_{BCC}}} = \frac{2V_{BCC}}{V_{FCC}}$$

20. Correct answer is (b)

We know that, for FCC atomic radius is given by

$r = \frac{a}{2\sqrt{2}} = \frac{4}{2\sqrt{2}} = 1.414$ Å

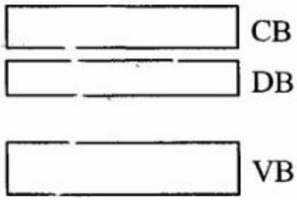
21. Correct answer is (b)

When Si is doped with group V elements like P, then at each P centre there is extra electron which constitute a donor band that lies close to empty corduction band.

VB = Valence band,

DB = Donor band,

CB = Conduction band



22. Correct answer is (a)

$$d_{hkl} = \frac{a}{\sqrt{h^2 + l^2 + k^2}}$$

$d_{110} = \frac{4.242}{\sqrt{1+1^2+0^2}} = 3$ Å

23. Correct answer is (a)

A = corners + face centers = $8 \times \frac{1}{8} + 6 \times \frac{1}{2} = 1 + 3 = 4$

And B = 4 (Full contribution in tetrahedral void)

24. Correct answer is (d)

X-ray diffraction give any structural information only for crystalline solids

25. Correct answer is (b)

d=160pm

$$\frac{d}{2} = \frac{a}{2\sqrt{2}} = \frac{r}{1}$$

$\Rightarrow a = d\sqrt{2}$

$V = a^3 = (d\sqrt{2})^3 = 2\sqrt{2}d^3$

$= 2\times 1.44 \times (160\times 10^{-10} cm)^3$

$= 11583488 \times 10^3 cm^3$

$1.158 \times 10^{-23} cm^3$

$1.158\times 10^{-23} cm^3$ contains 4 atoms

$$\therefore \ 1cm^3 \ contains \ \frac{4}{1.158\times 10^{-23}} \ atoms = 3.45\times 10^{23} \ atoms$$

26. Correct answer is (c)

$$2\times \frac{a}{\sqrt{h^2+l^2+k^2}} \ sin\theta = n \ \lambda$$

$$2\times \frac{a}{\sqrt{3}} \ sin \ 30° = 2 \times 1Å$$

27. Correct answer is (d)

$$\cos\theta = \frac{h_1h_2 + k_1k_2 + l_1l_2}{\sqrt{h_1^2+k_1^2+l_1^2}\sqrt{h_2^2+k_2^2+l_2^2}}$$

$$\cos\theta = \frac{2\times 0 + 0\times 0 + 1\times 1}{\sqrt{4+0+1}\sqrt{0+0+1}} = \frac{1}{\sqrt{5}} = \theta = 6.43$$

28. Correct answer is (c)

$$sin\theta = \frac{n\lambda}{2a}\sqrt{h^2+k^2+l^2}$$

$$sin\theta_1 = \frac{n\lambda}{2a}\sqrt{1+0+1}$$

$$sin\theta_2 = \frac{n\lambda}{2a}\sqrt{1+1+1}$$

$$\frac{sin\theta_1}{sin\ \theta_2} = \frac{\sqrt{2}}{\sqrt{3}} = \frac{1.414}{1.732} = 0.816 = 0.82$$

29. Correct option is (a)

Angle between (1 0 0) and (0. 1 0)

$$\cos\theta = \frac{0+0+0}{\sqrt{1}\sqrt{1}} \Rightarrow \theta = 90^0$$

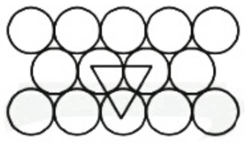
And angle between (100) and (011)

$$\cos\theta = \frac{0+0+0}{\sqrt{1}\sqrt{2}} \Rightarrow \theta = 90^0$$

30. Correct option is (b)

$$d_{hkl} = \frac{a}{\sqrt{h^2+l^2+k^2}} \Rightarrow \frac{a}{d} = \sqrt{h^2+l^2+k^2}$$

31. Correct option is (b)



From figure it is clear that each void is surrounded by three circles.

32. Correct option is (a)

$\mathrm{Sin}^2\theta$ at 2x, 4x, 6x, 8x

⇒ B.C.C

$$x = \frac{\lambda^2}{4a^2} \Rightarrow a = \frac{7}{2\sqrt{2}} = \frac{1.54}{2\times\sqrt{0.06}} = 3.14\,\dot{A}$$

33. Correct option is (b)

$$2\,\frac{a}{\sqrt{h^2+l^2+k^2}}\sin\theta = n\,\lambda$$

$$2\times\frac{40}{\sqrt{5}}\times\frac{1}{2} = 1\times\lambda$$

λ = 18 nm

34. Correct option is (c)

$$\rho = \frac{Zm}{a^3}$$

$$a = \left(\frac{Zm}{\rho}\right)^{\frac{1}{3}} = \left(\frac{1\times2.7\times10^{-22}g}{10gcm^{-3}}\right)^{\frac{1}{3}} = 3\times10^{-3}cm = 3\text{ Å}$$

$$and,\qquad r = \frac{a}{2} = 1.5\text{ Å}$$

35. Correct option is (d)

Packing fraction $= \frac{4}{3}Z\pi\left(\frac{r}{a}\right)^3 = = \frac{4}{3}\times2\times3.14\times\left(\frac{\sqrt{3}}{4}\right)^3 = \frac{\sqrt{3}\pi}{8}$ [$r = \frac{a\sqrt{3}}{4}$]

36. Correct option is (a)

$d_{246} = \frac{d_{123}}{2} = \frac{3.12}{2} = 1.56nm$, $d_{369} = \frac{d_{123}}{3} = \frac{3.12}{3} = 1.04$nm

37. Correct option is (a)

In FCC fraction of volume occupy=74%=0.74

$$\frac{\pi\sqrt{2}}{6} = \frac{3.14\times1.414}{6} = \frac{4.43996}{6} = 0.7399 = 0.74.$$

38. Correct option is (a)

$2d\sin\theta = n\lambda$

$2\frac{a}{\sqrt{h^2+l^2+k^2}}\sin 90^0 = 1\times0.154$ {for first order reflection n = 1}

$$2\frac{a}{\sqrt{0+0+4}} = 0.154\,nm$$

$$2\times\frac{a}{2} = 0.154nm \Rightarrow a = 0.154nm$$

$$\rho = \frac{Zm}{N_A a^3} \Rightarrow 4\times10^4 kgm^{-3} = \frac{4\times M}{6.023\times10^{23}\times0.154\times0.154\times10^{-27}m^3}$$

M= 22

39. Correct option is (b)

(111) = all odd

(222)= all even

40. Correct option is (a)

$\sin^2\theta = (h^2 + l^2 + k^2)$x where x = $\frac{n^2\ \lambda^2}{4a^2}$

a= $\frac{n\,\lambda}{2\sqrt{x}}$ …….(i)

for (200), $\sin^2\theta = 0.18 = 4x = 0.18$

x= 0.045

from equation (i)

$$a = \frac{1\,\lambda}{2\sqrt{0.045}} = \frac{\lambda}{0.4}$$

41. Correct option is (b)

From braggs equation , 2d sin θ =n λ

$\sin\theta = \frac{n\,\lambda}{2d}$

On squaring both sides , we get

$\sin^2\theta = \frac{n^2\ \lambda^2}{4d^2}$ ………(i)

inter planar distance $\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$

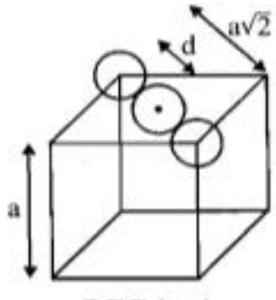
for tetragonal crystal sydrem , a = b $\neq c$

$\frac{1}{d^2} = \frac{h^2+k^2}{a^2} + \frac{l^2}{c^2} \Rightarrow \frac{c^2(h^2+k^2)+l^2a^2}{a^2c^2}$

Put $\frac{1}{d^2}$ in equation (i), we get $\sin^2\theta = \frac{\lambda^2}{4a^2c^2}\ [a^2(h^2+k^2) + c^2l^2]$

42. Correct option is (a)

In face central cubic crystal system we observed nearest neighour distance= d



FCC lattice

2d= a$\sqrt{2}$

$$d = \frac{a\sqrt{2}}{2} = \frac{a}{\sqrt{2}}$$

43. Correct option is (b)

The plane is parallel to c-axis, therefore, OC = ∞(intercept on z-axis)

The intercept on X-axis, OA=4a

The intercept on Y-axis, OB=2b.

	X	Y	Z
Intercept	4a	2b	∞
Reciprocal	$\frac{1}{4a}$	$\frac{1}{2b}$	$\frac{1}{\infty} = 0$
Multiply by a,b,c	$\frac{1}{4}$	$\frac{1}{2}$	0
Multiply by L.C.M	1	2	0

Therefore, the miller indices of plane are (1 2 0)

44. Correct option is (b)

Wavelength of X-rays, λ=173 pm, plane (111)

Simple cubic, θ= 30°, order n = 1

From Bragg's law,

$2d\ \sin\theta = n\lambda$ .....(i)

and $d = \frac{a}{\sqrt{h^2+l^2+k^2}}$ .....(ii)

Combining equations (i) and (ii), we get

$$a = \frac{n\lambda}{2d\ \sin\theta}\sqrt{h^2+l^2+k^2} = \frac{1\times 173}{2\times \sin 30^0}\sqrt{1^2+1^2+1^2} = \frac{173}{2\times\frac{1}{2}}\times\sqrt{3} = 299.645 \approx 300pm$$

45. Correct option is (c)

Iron = BCC

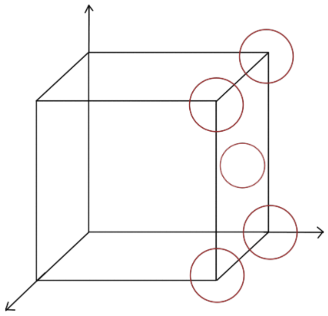
(h+k+l) =even for the planes in XRD data = 1st plane ⇒ (110), 4th plane ⇒ (220)

2nd plane ⇒ (200) , 5th plane ⇒ (310), 3rd plane ⇒ (211) , 6th plane ⇒ (222)

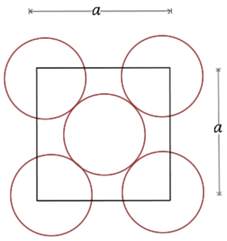
46. Correct option is (c)

CCP = FCC

(i) (1 0 0) plane



(1 0 0) plane



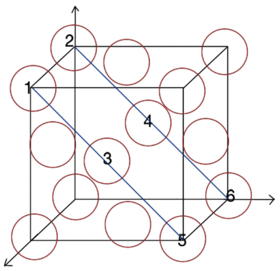
(1 0 0) plane

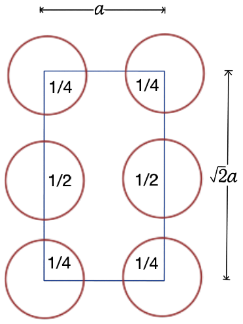
Number of atoms on the plane = 4x1/4 + 1×1=2

(For plane atoms are treated as disc)

Area of plane= a^2 . Therefore, the number of atom per unit area = $2/a^2$

(ii) (1 1 0) plane:



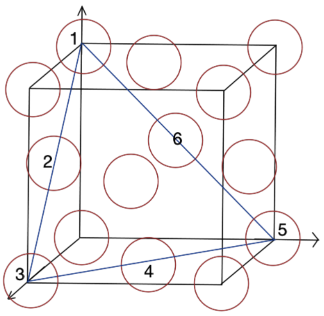


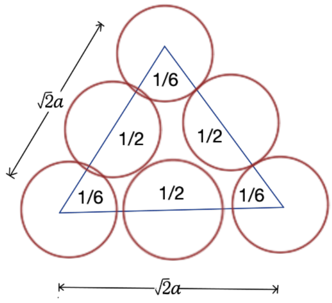
Number of atoms=4 × 1/4 + 2×1/2= 2 atoms

Area of plane $(\sqrt{2}a)\times(a)=\sqrt{2}a^2$

Therefore, number of atoms per unit area= $\frac{2}{\sqrt{2}a^2}=\frac{\sqrt{2}}{a^2}=\frac{1.414}{a^2}$

(iii) (111) plane:





Number of atoms 3×1/6 + 3×1/2= 2 atoms

Area of the plane= $\frac{\sqrt{3}}{4}\times\left(\sqrt{2}a\right)^2 = \frac{\sqrt{3}}{4}\times(2a)^2 = \frac{\sqrt{3}}{2}\times a^2$

Number of atoms per unit area= $\frac{2}{\frac{\sqrt{3}}{2}a^2} = \frac{4}{\sqrt{3}a^2}$

Number of atoms per unit area

(100)$\Rightarrow \frac{2}{a^2}$

(110)$\Rightarrow \frac{\sqrt{2}}{a^2} = \frac{1.414}{a^2}$

(111)$\Rightarrow \frac{4}{\sqrt{3}a^2}$

(111) > (100)> (110)

47. Correct option (d)

Using density formula, $\rho = \frac{z.M}{N_A.a.b.c}$

Putting, z = 16

M = 244 g mol^{-1}

a = 620pm = 620×10^{-10}cm

b = 480pm = 480×10^{-10}cm

c = 1100pm = 1100×10^{-10}cm

$$\rho = \frac{16\times244}{6.023\times10^{23}\times620\times10^{-10}\times480\times10^{-10}\times1100\times10^{-10}}$$

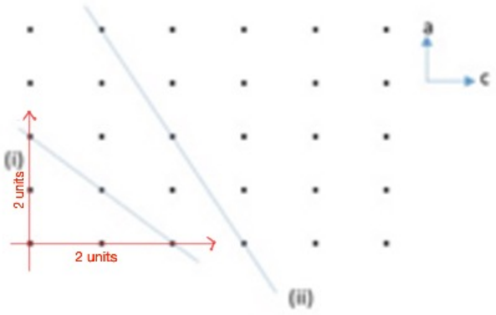
We get, Density (ρ) ≈ 20.46 g/cm^3

48. Correct option (d)

Since the image shown is a-c plane and it does not have b axis, thus intercepts along b axis will be considered ∞

We will use general notation to represent intercepts along a, b and c axes as (a,b,c)

The intercepts made by line (i) are $(2, \infty, 2)$

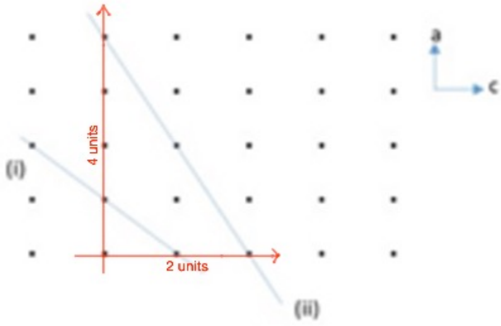


Thus miller indices corresponding to it will be,

$\Rightarrow \left(\frac{1}{2}, \frac{1}{\infty}, \frac{1}{2}\right)$

$\Rightarrow (1, 0, 1)$

The intercepts made by line (ii) are $(4, \infty, 2)$



Thus miller indices corresponding to it will be,

$\Rightarrow \left(\frac{1}{4}, \frac{1}{\infty}, \frac{1}{2}\right)$

$\Rightarrow (1, 0, 2)$

2

Chemical Kinetics

Hints & Solutions

1. CORRECT ANSWER –(A)

If the rate constants K1 and K2 at temp. T1 and T2 respectively and φ is the temp. coefficient , then these are related by the expression k2 =K1 $(\varphi)^{\Delta T/10}$ where, Δ T = T2-T1.

Here , K1 = 2.66* $10^{-3s}S^{-1}$ and K2= 2.2*$10^{-1}S^{-1}$

T1= 120K and T2= 360K.

So, 2.2 * 10^{-1}/2.66*10^{-3}=$(\varphi)^{24}$ or φ = 1.2

Now, at temp. 240K , rate constant (K3)= 2.66* 10^{-3}*$(1.2)^{12}$ = 2.4*$10^{-2}S^{-1}$

2. CORRECT ANSWER –(A)

RDS step - A_2+C $\rightarrow$ P(K3)

Rate of the reaction =K3[A_2][C] ..... (1)

As A_2 and C are not apperaring in the reaction, so they are acting as intermediates. As equilibrium is fast so concentration of [A_2] and [C] can be determined by using equilibrium constants.

K1= [A_2]/$[A]^2$ or, [A_2]=K1$[A]^2$ ...... (2)

K2 = [C]/[A][B]

$\Rightarrow$ [C]= K2 [A][B] .... (3)

From equation (1),(2) and (3), we get dp/dT = K3*k1*k2*$[A]^3$[B].

3.

QUANTA POINT

CONC.	TIME
0.1(M)	t1=1 hr
.08(M)	t2=2hr
0.067(M)	t3=3hr

Above data satisfies second order equation. $k = \frac{1}{\Delta t}[\frac{1}{[A]t2} - \frac{1}{[A]t1}]$

From data (i) and (ii) ,$k = \frac{1}{2-1}\left[\frac{1}{0.08} - \frac{1}{0.1}\right]$ = 2.5$M^{-1}hr^{-1}$

From data (i) and (iii) , $k = \frac{1}{3-1}[\frac{1}{0.067} - \frac{1}{0.1}]$=2.5 $M^{-1}hr^{-1}$.

As the value of k is constant so the order of the reaction =2.

4. Correct answer is (a).

Heavier isotope contains heavier bonding. Heavier the bonding reaction rate slow. But in lighter isotope bonding is weak, so reaction rate is faster.

5. Correct answer is (c).

When equilibrium reactions are disturbed from their equilibrium condition via either T-Jump or pH Jump then measurement of relaxation time leads to the study of reaction rate.

6. CORRECT ANSWER-(A).

A→ P is ZERO order reaction.

$[A]_t=[A]_0- kt$

So , $kt= [A]_0-[A]_t$

⇨ $Kt_{1/2}= [A]_0- \frac{[A]0}{2}$

⇨ $t_{1/2} = [A]_0/2K$.

7. Correct option (d)

Acetaldehyde (CHCHO) $\xrightarrow{k}$ product , rate = k$[CH_3CHO]^2$

In terms of partial pressure , rate = k$P^2_{CH_3CHO}$

Integral rate law expression is $\frac{1}{P_{CH_3CHO}} - \frac{1}{P^0_{CH_3CHO}} = kt$

Or, $t_{1/2} = \frac{1}{k\times P^0_{CH_3CHO}}$

Since given t = 400sec and $P^0_{CH_3CHO} = 250$

400sec = $\frac{1}{k\times 250Torr} \Rightarrow k = 10^{-5} torr^{-1}s^{-1}$

$P^0_{CH_3CHO} = 200$

$t_{1/2} = \frac{1}{k\times P^0_{CH_3CHO}} = \frac{1}{10^{-5}\times 200} = 500\ sec$

8. Correct option (c)

From enzyme kinetics R = $\frac{K_2[E]_0[S]_0}{K_M+[S]_0}$

$$\frac{1}{R} = \underset{\substack{\downarrow \\ \text{Slope}}}{\left(\frac{K_m}{k_2[E]_0}\right)}\frac{1}{S_0} + \underset{\substack{\downarrow \\ \text{Intercept}}}{\frac{1}{K_2[E]_0}}$$

Catalytic efficiency $= \frac{k_2}{k_m} = \frac{1}{\frac{km}{k_2}\times\frac{[E]_0}{[E]_0}} = \frac{1}{Slope \times[E]_0} = \frac{1}{40\times2.5\times10^{-9}} = 10^7$

9. Correct option (d)

Optional density (O.D)= Absorbance = $\log\left(\frac{1}{T}\right) = \in cl$ ……(1)

Solution A : T=0.5 ; O.D = $\log\left[\frac{1}{0.5}\right] = log2 = 0.301$

From equation 1 , $\in\times0.1\times1 = 0.301 \Rightarrow \in = 3.01\ mol^{-1}dm^3cm^{-1}$

Solution B : Optional density (O.D)= Absorbance = $\log\left(\frac{1}{T}\right) = \in cl = 3.01 \times0.5\times0.1 = 0.1505$

Solution C : Optional density (O.D)= Absorbance = $\log\left(\frac{1}{T}\right) = \log\frac{1}{0.1} = 1$

Therefore , optical density order c> a > b

10. CORRECT ANSWER- (D)

We know that Arrhenious Equation- $k=Ae^{-Ea/RT}$ …(1)

Given: $k=5.4 *10^{11}e^{-50}$ …(2)

Comaparing eqn. 1 and 2,

Ea/RT = 50

⇨ Ea =50 RT =50*8.314 J K^{-1} mol^{-1}(300K) = 124710 J mol^{-1}

11. CORRECT ANSWER – (C)

$K_{overall}=k_2(k_1/k_4)^{1/2}$

Taking log on both sides

$\log K_{overall}= \log k_2+ \log(k_1/k_4)^{1/2}$

⇨ $\log K_{overall}= \log k_2+ ½ \log k_1 - ½ \log k_4$

$(E_a)_{overall}= E_a(2)+ ½ E_a(1)- ½ E_a(4)$

12. CORRECT ANSWER- (C)

$v = \frac{Vmax[S]}{[S]+km}$ [where , $v_{max} = k_3 [E_0]$]

$v= \frac{k3\ [E]0[S]}{[S]+km}$ => $v/[E]_0[S] = \frac{k3}{[S]+km}$

⇨ $\frac{v}{[E]0[S]}[[S]+k_{m]}=k_3$

⇨ $\frac{v[S]}{[E]0[S]} + \frac{vkm}{[E\}0[S]} = k3$

⇨ $\frac{vkm}{[E]0[S]} = k3 - \frac{v}{[E]0}$

⇨ $\frac{v}{[E]0[S]} = \frac{k3}{km} - \frac{V}{[E]0km}$

⇨ $\frac{v}{[E]0[S]} = 1.4 * 10^{12} - \frac{10^4v}{[E]0}$

⇨ $\frac{k3}{km} = 1.4 * 10^{12}$

⇨ $1/km = 10^4$

⇨ $km = 10^{-4}$

⇨ $\frac{k3}{10000} = 1.4 * 10^8$

⇨ $k3 = 1.4 * 10^8$

13. Correct option (a)

Equilibrium is maintained between reactants and the activated complex

A + B ⇋ $X^{\neq} \rightarrow P$

14. Correct option (d)
15. Correct option (d)

$$r_0 = 15.3dpm\,; r = 14.2dpm$$

Rate at any time ∝ $Number\ of\ atoms$

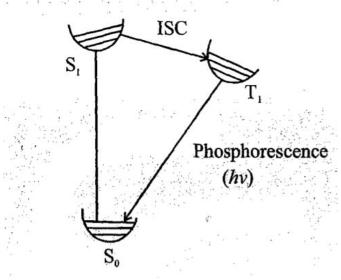
$$\frac{r_0}{r} = \frac{N_0}{N} = \frac{15.3}{14.2}$$

t=$\frac{2.303\times t_{1/2}}{0.693}$ log $\frac{N_0}{N} = \frac{2.303\times 5730}{0.693}\ log\frac{15.3}{14.2} = 617\ years$

16. Correct option (a)

"Phosphorescence" is in a transfer from triplet state to singlet which can be represented as

$$T_1 \rightarrow S_0 + hv$$



17. Correct option (d)

A= $2 - log_{10}T\%$

A=$2 - log_{10}50\%$

A= $\in cl \;\; \Rightarrow 0.301 = \in\times 10^{-4}\times 0.5 \Rightarrow \in = 6020M^{-1}cm^{-1}$

18. CORRECT OPTION-(B)

Quarter life is the time in which the concenration decreases to 1/4th of its initial value. Rate law expression for the first order reaction is –

Kt= ln (a/a-x) …(1)

Therefore, x=3a/4 ;t=$t_{1/4}$

So,$kt_{1/4}$ = ln$\left\{\frac{a}{a-\frac{3a}{4}}\right\}$

=ln$\left\{\frac{a}{\frac{a}{4}}\right\} = ln4$

⇨ $t(\frac{1}{4}) = \frac{ln4}{k}$

19. Correct answer-(C)

Smaller the volume greater will be the chances of collision probability and so the activation energy of the reaction will decrease.

20. Correct option (b)

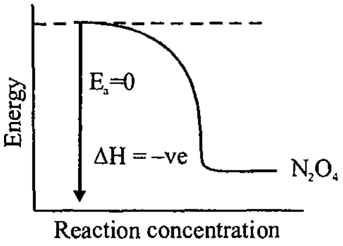
At low pressure Langmuir-Hinshelwood mechanism follows first order kinetics

K = $\frac{2.303}{t} log_{10} \frac{P_0}{P_t} = \frac{2.303}{10} \log_{10} \frac{10^{-2}}{10^{-4}} = 0.4606\, min^{-1}$

21. CORRECT ANSWER-(b)

For atom recombination reaction, there is a relatively small amount of rearrangement of energy among the various defracts in the activated complex. Consequently, $\Delta S^{\#}$ is expectedto have a small negative value. Such process occurs with zero activation energy and negative enthalpy change e.g. dimerization of nitric oxide.

22. CORRECT OPTION-(B)



Kt= ln(c_0/c_1)

⇨ K= $\frac{1}{75} \ln\left(\frac{34500}{21500}\right)$

⇨ $K = 6.3049 * 10^{-3}$

⇨ $t\left(\frac{1}{2}\right) = \frac{0.693}{k} = 0.693/(6.3049 * 10^{-3})$

⇨ $t\left(\frac{1}{2}\right) = 110 min$

23. CORRECT OPTION-(A)

When the chain mechanism exceeds the chain termination, it results in uncontrolled step, chain reaction that ultimately results in explosion.

For the nth order, $t_{1/2}=[A_0]^{1-n}$

Therefore, for n=2.5, $t_{1/2} \propto [A_0]^{1-2.5}$ or, $t_{1/2} \propto [A]_0^{-3/2}$

Rate law expression is, r= $k_1k_3[A]^2/(k_2[A]+k_3)$

For low pressure, $k_2[A]>>k_3$

So, r=$k_1k_3[A]/k_2$

$$A + A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} A^* + A \text{ and } A^* \xrightarrow{k_3} P$$

R= $k_3[A^*]$ => $[A^*]$=r/k_3= $\frac{}{k2[A]+k3}$

So, r= $\frac{k1k3[A]^2}{k2[A]+k3}$

24. Given reaction A→P ; [A]=1.0, 0.5, 0.33, 0.25 mol dm–3 at t = 0, 1, 2 and 3 seconds, respectively.

So, we observe that when concentrations becomes half the half life becomes double.

$t_{1/2}$=1/ak =>k= 1/a$t_{1/2}$

so, order=2.

25. CORRECT ANSWER-(d)

In the lindermann mechanism, rate equation can be written as:

$$\frac{d[\text{product}]}{dt} = \frac{k_2k_1[A]^2}{k_{-1}[A]+k_2}$$

At low conc. Of [A], $k_{-1}[A] << k_2$, so ,$\frac{d[product]}{dt} = \frac{k2k1[A]^2}{k2}$
So the order of the reaction is- 2.

26. CORRECT ANSWER- (a)
Acc. To Arrhenious equation-: $\ln k = \ln A - E_a/RT$
So, $\ln k \propto 1/T$; lnk varies linearly decreasing wrt 1/T.

27. Correct option (c)
For c, r= k$[AB][B_2]$
Since, rate is given by slowstep.
Therefore , this mechanism is consistent with given rate law.

28. Correct option (a)
A, T= 0.50 , c= 0.1m, b= 1cm
B, A= 0.01761, c = 0.1m, b= 1cm
For solution a,
Ab$\in = -logT = -\log(0.5) = 0.3010$
Therefore , abs of simultaneous solution of (A) and (B) = 0.3010 + 0.1761= 0.4771
Therefore , required transmittance = $10^{-Ab\in} = 10^{-0.4771} = 33.3\%$

29. According to transition state theory, for activated complex, one of its vibrational degree of freedom is being converted into translational degree of freedom. Therefore, required vibration degree of freedom (3N-6)-1 = 3N-7.

Correct answer is (c)
30. K = A +$e^{-\mathrm{Ea}/\mathrm{kT}}$ (Arrhenius equation)
In K = In A – Ea/ RT
ln K = $\left(\frac{\mathrm{Ea}}{\mathrm{RT}}\right)\left(\frac{1}{T}\right)$ + In A
y = mx + c
Clearly Ink decreases linearly as 1/T increases. Correct answer is (a)

31. CORRECT ANSWER(C)
From arrhenious equation, we have
$\ln\left(\frac{k2}{k1}\right) = \frac{Ea}{R}\left(\frac{1}{T1} - \frac{1}{T2}\right) = \left(\frac{Ea}{R}\right)\frac{(T2-T1)}{T1T2}$
$Ea = \frac{RT1T2}{T2-T1}\ln\left(\frac{k2}{k1}\right) = 2calK^{-1}mole^{-1} * 500K * \frac{510K}{510-500} ln3 = 55kcalmole^{-1}$

32. CORRECT ANSWER- (B)
r= $kP^{a}_{NO}P_{H2}{}^{b}$
From experiment 1, on doubling pressure NO rate becomes 4 times,so, a=2
From experiment2, on doubling the pressure of H_2 rate becomes almost double, so b=1.
So, r=$kP_{No}{}^{2}P_{H2}{}^{1}$

33. CCORRECT OPTION-(D)
Steady state approximation for consecutive reaction
P ---^{k1}-----> Q---^{k2}---->R

When the first step is slow and the second step is fast.

34. CORRECT ANSWER(D)
Lineweaver burk plot: (1/r vs 1/[S])
$slope = \frac{km}{(r)max}$; $r_{max}=k_2[E]_0$
And intercept=$1/r_{max}$
TON=k_2.
Given: K_2= 5000M^{-1}s
⇨ $\frac{1}{rmax} = 500M^{-1}s$
⇨ $(r)max = \frac{1}{5000}$
⇨ $K_{2*}[E]_0=\frac{1}{5000}$
⇨ $TON * 1 * 10^{-9}M = \frac{1}{5000}$
⇨ $TON = 2 * 10^5$.

35. Correct option (c)

$$\tau_f = \frac{\phi_f}{k_f}$$

$$\tau_f = \frac{1}{k_f + k_{IC} + k_{ISC}}$$

Given , $k_{IC} + k_{ISC} = 1.2\times10^8 \sec^6 \, and \, \tau_f = 5\times10^{-9}sec$

Therefore , (ii) ⇒ $5\times10^{-9}\sec = \frac{1}{K_f+(1.2\times10^8\sec^{-1}.)}$

$$K_f + (1.2\times10^8\sec^{-1}.) = \frac{1}{5\times10^{-9}sec}$$

$$K_f = \frac{10}{5}\times10^{-1}\times10^9\sec^{-1} - 1.2\times10^8\sec^{-1}.$$

$= 2\times10^8\sec^{-1} - 1.2\times10^8\sec^{-1}. = 0.8\times10^8\sec^{-1}.$

Therefore , (i) ⇒ $\phi_f = \tau_f\times K_f = (5\times10^{-9}sec)\times(0.8\times10^8\sec^{-1}.) = 0.4$

36. Correct option (b)
A= In$\left(\frac{c_0}{c_t}\right)$, $kf = \ln\left(\frac{[A]_0}{A_t}\right)$
In$\left(\frac{[A]_t}{[A]_0}\right) = -kt$
Therefore a straight line with a negative slope passing through origin.

37. CORRECT OPTION(D)
$\frac{1}{V} = \frac{km}{(v)\max[S]0} + \frac{1}{vmax}$ {Lineweaver burk plot }
$slope$ =$K_m/v_{max}=k_m/k_2[E]_0$=40 s(given)
Catalytic efficiency= $k_2/k_m = 1/40[E]_0 = 1/(40*2.5*10^{-6}) = 10^4$ $Lmol^{-1} sec^{-1}$

38. CORECT OPTION(D)

$2NO(g) + Cl_2(g) \rightarrow$ Non –linear TS $\rightarrow 2NOCl$

$$A \propto \frac{T^{\frac{3}{2}}}{T^{\left(\frac{3}{2}\right)}\,T.T^{\frac{3}{2}}.T} = \frac{1}{T^{\frac{7}{2}}}$$

⇨ $A \propto T^{-7/2}$

39. CORRECT ANSWER (C)

Since , $\log(k/k_c) = 2Z_AZ_B\sqrt{I}$

⇨ $0.3 = 2*(1/2)*n*\sqrt{.01}$

⇨ $n = 30*10^{-2}/10^{-1}$

⇨ n=3.

40. Correct option (c)

$A+B \leftrightharpoons AB$, ΔH

$AB+C \rightarrow D$, E_0

ΔH is the enthalpy change for the reaction and E_0 is the activation energy , for second reaction . So, the activation energy of overall reaction is $E_0 + \Delta H$

41. Limitations of Beer's law are

Solution must be dilute, radiation must be monochromatic, temperature should not vary largely. Analyte molecule should not undergo any kind of association or dissociation.

Refractive index of medium should not change.

Correct answer is (a)

42. CORRECT OPYION (C)

$K = AT^2e^{-(E0/RT)}$

⇨ $\ln k = \ln A + 2\ln T - E_0/RT$

⇨ $\frac{d}{dT}\ln k = 0 + \frac{2}{T} + \frac{(E)0}{RT^2}$

⇨ $but, \frac{d}{dT}\ln k = \frac{(E)0}{RT^2}$

⇨ $\frac{2}{T} + \frac{(E)0}{RT^2} = \frac{Ea}{RT^2}$

⇨ $Ea = RT^2\left\{\frac{2}{T} + \frac{(E)0}{RT^2}\right\}$

⇨ $Ea = 2RT + (E)_0$

43. CORECT OPTION-(A)

Rate of formation of Z=(3/2) rate of formation of A

$=(3/2)*2*10^{-4} = 3*10^{-4}$

44. CORRECT OPTION(C)

$CH_4(g) + 2H_2O(g) \rightleftharpoons CO_2(g) + 4H_2(g)$ (K1)

$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$ (K2)

Equation subtracting (1) from (2), we get

$CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g)$

And the equilibrium const = (K1/K2)

45. CORRECT OPTION-(B)

log(k/k$_c$)= $2Z_AZ_B\sqrt{I}$

Given: $2AZ_AZ_B\sqrt{I}$ =-4 *0.51*$\sqrt{I}$
Z_AZ_B=-2.

46. Correct answer is (d)
-logT_1 = $\in cx_1$
-log T_2 = $\in cx_2$
Substitution (2) from (1)

$$\frac{logT_2}{logT_1} = \frac{x_2}{x_1} \Rightarrow logT_2 = \frac{3}{1}\times log\left(\frac{50}{100}\right) = 3\,[log1 - log2] = 3\times(-0.3010)$$

T_2 = $10^{-3\times0.3010} = \frac{1}{10^{3\times0.3010}} = \frac{1}{10^{0.9030}}$

$= \frac{1}{7.99} = \frac{1}{8} = 0.125\times100 = 12.5\%$

47. Correct answer is (d)
Increase of intensity of light used in fluorescence as the fluorescence lifetime increases .Molar absorptivity increase absorbance which further enchances absorbance with further enchances fluorescence CORRECT OPTION-(b)
d[B]/dt= Rate of formation of A- Rate of formation of B
$= 2k_1[A]-2k_{-1}[B]^{-2}-k_2[B]$.

48. Correct answer is (d)

A –A = $\frac{N_Ak_BT}{h}\frac{q^{\#}}{q_{A-B}q_{CDE}} = \frac{N_Ak_BT}{h}\frac{(q_t^3q_rq_v^{11})_{nonlinear}}{(q_t^3q_rq_v^{11})_{linear}(q_t^3q_rq_v^3)_{linear}}$

$$\frac{N_Ak_BT}{h}\frac{q_v^7}{q_t^3q_{r(linear)}}$$

$\frac{N_Ak_BT}{h}\frac{[T^0]^7}{T^{3/2}\,T} \Rightarrow A \propto \frac{T}{T^{\frac{3}{2}}\,T} \Rightarrow A \propto T^{-3/2}$

A$\propto T^{-\frac{3}{2}}, A \propto T^{-1.5}$

49. Correct answer is (d)
Rate of reaction , r = $k_2[C_2H_5]^2$
SSA on $C_2H_5, Rate\ of\ formation\ of C_2H_5, = rate\ of\ deformation\ of\ C_2H_5,$
$2k_1I_a = 2k_{-1}\,[C_2H_5]^2 + 2k_2\,[C_2H_5]^2$
$k_1I_a = (k_{-1} + k_2)[C_2H_5]^2$
$[C_2H_5]^2 = \frac{k_1I_a}{k_{-1}+k_2}$
Therefore , from equation (1),
r=$\frac{k_2k_1I_a}{k_{-1}+k_2} \Rightarrow r \propto I_a$

50. *Correct option* (d)

$$\frac{d[B]}{dt} = Rate\ of\ formation\ of\ B - Rate\ of\ deformation\ of\ b$$

$2k_1[A] - 2k_{-1}[B]^{1/2} - k_2[B]$

51. CORRECT OPTION-(D)
$q_v = 1/(1- e^{hv/kT})$ for loose vibration
$q_v = \frac{1}{1-1+\frac{hv}{kT}} = \frac{kT}{hv}$

52. CORRECT OPTION-(B)
r= (r) max $\frac{[S]}{[S]+km} = 2 * 10^{-3} * 1 * \frac{10^{-6}}{1*10^{-6}+10^{-6}} = 10^{-3}\ s^{-1}$

53. CORECT OPTION-(B)

$$A + A \underset{k_a'}{\overset{k_a}{\rightleftarrows}} A^* + A, \quad A^* \xrightarrow{k_b} P$$

So, r= $k_a k_b[A]^2/(k'_a[A]+ k_b)$
R=$k_{obs}[A]$
With $k_{obs}=k_a k_b/k'_a$ at high P
$= k_a[A]$ at low P
So, $k_{obs}= k_a [A]$
$2= k_a \times 1 \Rightarrow k_a = 2\ atm^{-1}s^{-1}$

54. Correct answer is (c)
C_t vs t straight line is observed for 0 , order and $\frac{1}{c_t}$ $vs\ t$ straight line is observed for second order

55. CORRECT OPTION-(A)
$\frac{R1}{R2} = \left(\frac{C1}{C2}\right)^n$

$$\log\left(\frac{R1}{R2}\right) = n\log\left(\frac{C1}{C2}\right)$$

$$n = \frac{\log R1 - \log R2}{\log C1 - \log C2}$$

56. CORRECT OPTION(C)
The rate law has only NO_2F ; so the reactant for the rds step will be NO_2F.
$NO_2F \rightarrow NO_2 + F$

57. CORRECT OPTION –(B)
Entropy of activation for bimolecular reaction is negative. Therefore,(d) is incorrect.
Here, positive salt effect. Therefore, (c) is incorrect.
Increase of dielectric constant increases rate constant.

58. CORRECT OPTIION (C)
If experimental rate s greater than maximum rate using collision theory then impact parameter must be greater than sum of radii of reactants.

59. CORRECT OPTION (A)

For a 3rd order reaction,

$$kt = \frac{1}{2}\left(\frac{1}{(a-x)^2} - \frac{1}{a^2}\right)$$

For half life time,t→$t_{1/2}$,a-x=a/2

So, $kt_{1/2}=\frac{1}{2}\left\{\frac{4}{a^2} - \frac{1}{a^2}\right\} = \frac{3}{2a^2}$

60. Correct option (d)

$\ln\left(\frac{k_2}{k_1}\right) = \frac{E_a}{R}\left[\frac{T_2-T_1}{T_1T_2}\right]$

$\ln\left(\frac{k_{600}}{k_{300}}\right) = \frac{49.8\times1000Jmole^{-1}}{8.4Jmole^{-1}K^{-1}} \left[\frac{(600-300)K}{300K\times600K}\right]= 10$

$$\frac{k_{600}}{k_{300}} = e^{10}$$

61. Correct option (c)

$K = \frac{k_BT}{h} e^{\frac{-\Delta H^\#}{RT}} e^{\frac{\Delta S^\#}{R}}$

$\frac{K}{T} = [\frac{k_B}{h} e^{\frac{\Delta S^\#}{R}}] e^{\frac{-\Delta H^\#}{RT}}$

$$\ln\left(\frac{k}{T}\right) = \ln\left[\left(\frac{k_B}{h}\right)e^{\frac{\Delta S^\#}{R}}\right] - \frac{\Delta H^\#}{R}\left(\frac{1}{T}\right)$$

y = c+mx

62. Correct option (d)

Rate of production of D

r=$k_2[A][C]$ …….1

SSA on C

$2K_1[A][B] = 2K_{-1}C^2 + K_2[A][C] = [C]\left[2K_{-1}[C] + k_2[A]\right]$

$[C] = \frac{2k_1[A][B]}{[2K_{-1}[C]+k_2[A]]}$ ………2

Therefore , $k_2[A] \ll K_{-1}[C]$

(2)⇒ $[C] = \left(\frac{k_1}{k_{-1}}\right)^{\frac{1}{2}} [A]^{\frac{1}{2}}[B]^{\frac{1}{2}}$

(1)⇒ $r = k_2\left(\frac{k_1}{k_{-1}}\right)^{\frac{1}{2}} [A]^{\frac{3}{2}}[B]^{\frac{1}{2}}$

on doubling the concentration of A,rate of formation of D will change $2\sqrt{2}$ times.

63. Correct option (a)

Pre exponential factor in collision theorey , A ∝ $\frac{\sigma^2}{\sqrt{\mu}}$

$$\frac{A_2}{A_1} = \left(\frac{\sigma_2}{\sigma_1}\right)^2 \left(\frac{\mu_1}{\mu_2}\right)^{1/2}$$

$$\frac{A_2^2}{A_1^2} = \left(\frac{\sigma_2}{\sigma_1}\right)^4 \left(\frac{\mu_1}{\mu_2}\right) \dots\dots..1$$

$$here\ ,\sigma_1 = \sigma_2 = 0.4$$

(1) ⇒ $\frac{A_2^2}{A_1^2} = \left(\frac{\mu_1}{\mu_2}\right)$

$$\mu_1 = \frac{5\times20}{25} = 4$$
$$\mu_2 = \frac{10\times10}{20} = 5$$
$$\frac{A_2^2}{A_1^2} = \frac{4}{5}$$

64. Correct option (d)

$[X^+] + [Y^{2-}]+[H^+] \leftrightharpoons [XYH^\#] \rightarrow Product$

$$\frac{k}{k_0} = \frac{\gamma_{X^+}\gamma_{Y^{-2}}\gamma_{H^+}}{\gamma_{XYH^\#}}$$
$$log\,\frac{k}{k_0} = -B\sqrt{I}[(+1)^2 + (-2)^2 + (+1)^2 - (0)^2]$$
$$= -B\sqrt{I}[1 + 4 + 1\,]$$
$= -6B\sqrt{I}$ ………..1

$log\left(\frac{k}{k_0}\right)_1 = -6B\sqrt{I_1}$ …………….2

$log\left(\frac{k}{k_0}\right)_2 = -6B\sqrt{I_2}$

$here\,, I_1 = 16\; and\; I_2 = 4$

1-2 = $log\left(\frac{k_2}{k_1}\right)_2 = -6B[\sqrt{I_2 - I_1}$

$$log\left(\frac{k_4}{k_{16}}\right)_2 = -6B\left[\sqrt{4} - \sqrt{16}\right] = 12B$$

65. CORRECT OPTION (A)

$K= Ae^{-Ea/RT}$

At very high temp. T→ ∞.

$K= Ae^{-Ea/R\infty} = Ae^0 =A$

66. CORRECT OPTION-(C)

With the increase in time the slope will decrease.

67. CORRECT OPTION-(C)

Rate of removal ofHI=$k_1[H][HI]+I_0$ ….(1)

Applying ssa on H^*, we get $I_a=k_1\,[H^*][HI]$

Therefore, eqn.(1) => $r=I_a$.

68. CORRECT OPTION-(A)

$\gamma_{max} =k_2\,[E]_0= 3.42*10^{4*}1*10^{-2} = 3.42 *10^2$ moldm^{-3} sec^{-1}

and TON=k_2=3.42*$_{10}{}^{4}$ s^{-1}

69. CORRECT OPTION-(A)

$\frac{k1}{A1} = e^{\frac{-E1}{RT}}$ …..(1)

$\frac{k2}{A2} = e^{-\frac{E2}{RT}}$ ……(2)

$\frac{2}{1} = \frac{k2}{A2} * \frac{A1}{k1} = e^{\frac{E1-E2}{RT}}$

$\frac{k2}{k1} * \frac{A1}{A2} > 1 => \frac{A1}{A2} > \frac{k1}{k2}$

70. CORRECT OPTION-(D)
Rate of formation of I=Rate of deformation of I
$k_1[A]=k_2[I]$
$[I]=(k1/k2)\ [A]$

71. CORRECT OPTION-(D)
Slope= $k_m/r_{max}= 300$ ….(1)
Intercept=$1/r_{max} =2*10^5$ …(2)
(1)/(2)=> $k_m = 1.5*10^{-3}$

72. From entry (1) and (2) ,order wrt B=1
From (3) and (4) , we get order wrt A=2
CORRECT OPTION (c)

73. CORRECT ANSWER-(a)

$$\frac{d[C]}{dt} = k2[C]^2$$

Equilibrium approximation, $\frac{k1}{k(-1)} = \frac{[L]^2}{[A][B]}$; $[C] = \left(\frac{k1[A][B]}{k(-1)}\right)^{\frac{1}{2}}$

$$\frac{d[D]}{dt} = \frac{k2(k1)^{\frac{1}{2}}}{k(-1)^{\frac{1}{2}}}\left[[A]^{\frac{1}{2}}[B]^{\frac{1}{2}}\right]^2 = \frac{k2(k1)^{\frac{1}{2}}}{k(-1)^{\frac{1}{2}}}[A][B]$$

$$\frac{d[D]}{dt} \propto [A][B]$$

74. CORECT OPTION-(A)
$E_0= 10^{-6}$ M; $k_{-1}/k_2=1000$; k1=?
Slope= 10^{-2} s; intercept= $10^2 M^{-1}s$
Michaelis menten equation is

$r = \frac{k2[E(0)][S]}{km+[S]}$ where $km = \frac{k(-1)+k(2)}{k(1)}$

$$\frac{1}{r} = \frac{km + [S]}{k2[E(0)][S]} = \frac{km}{k2[E(0)][S]} + \frac{1}{k2[E(0)]}$$

$$y = mx + c$$

$slope = \frac{km}{k2[E(0)]} = 10^{-2}$ ….(1)

$$Intercept = \frac{1}{k2[E(0)]} = 100$$

From eqn. (1) and(2)

$$km * 10^2 = 10^{-2}\ or, km = 10^{-4}$$

$$\frac{k(-1) + k2}{k1} = 10^{-4}$$

$$\frac{(1000k2 + k2)}{k1} = 10^{-4} \quad as, \frac{1}{k2 * 10^{-6}} = 100$$

$$k2 * \frac{1001}{k1} = 10^{-4}$$

$$k1 = 10^4 * \frac{1001}{10^{-4}} \quad as\ k(-1) = 1000k2$$

$$k1 = 10^8 * 1001 => k1 = 1.001 * 10^{11}$$

75. $\Delta E=E_b-E_f= 9.212RT$

CORRECT OPTION-(B)

$A_f=2A$, $A_b=A$, $k_{eq}=?$

Since, $k= Ae^{-Ea/RT}$

$K_f= A_f e^{-Ef/RT}$

$lnk(f) = \ln A(f) - \frac{E(f)}{RT}$ ….(1)

$\ln k(b) = \ln A(b) - \frac{E(b)}{RT}$ …. (2)

Subtracting equation (2) and (1)

$$lnk(f) - lnk(b) = \ln A(f) - \ln A(b) - \frac{E(f)}{RT} + \frac{E(b)}{RT}$$

$$\ln\left(\frac{k(f)}{k(b)}\right) = \ln\left(\frac{A(f)}{A(b)}\right) + \left(\frac{E(b) - E(a)}{RT}\right)$$

$$\ln k(eq) = log2 + \frac{9.212}{2.303} = log2 + 4 = 0.301 + 4 = 4.301$$

$$k(eq) = 10^{4.301} = 2 * 10^4$$

76. second-order reaction,

$k_2t = \frac{1}{c_t} - \frac{1}{c_0} \Rightarrow \frac{1}{c_t} = k_2t + \frac{1}{c_0}$

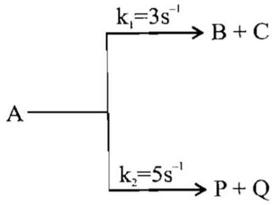
correct option (b)

77. Correct answer is (a)

$T_{1/2} \propto \frac{1}{a^{n-1}}$ [Given $t_{1.2} \propto \frac{1}{[A]_0^2}$]

n-1= 2, n=3

78. Correct answer is (a)



Percentage yield of P = $\frac{k_2}{k_1+k_2} \times 100 = \frac{5}{8} \times 100 = 62.5\%$

79. Correct answer is (b)

Fluorescence intensity on rate = 0.2 $[M^*]$

Applying S.S.A on M*

$I_{abs} = k_Q [Q][M^*] + 0.2[M^*]$

$[M^*] = \frac{\text{Iabs}}{k_Q [Q]+0.2}$

$I_f = \frac{0.2\, I_{abs}}{k_Q [Q]+0.2}$

$$\frac{1}{I_f} = \frac{k_Q}{0.2I_{abs}}[Q] + \frac{1}{I_{abs}}$$

y= mx+c

$$\frac{I}{I_{abs}} = 4 \Rightarrow I_{abs} = \frac{1}{4} = 0.25$$

80. k=0.2 Lmol^{-1}s^{-1}. It is a second order kinetics $t_{1/2} = \frac{1}{ak} = \frac{1}{0.05 \times 0.2} = 100$ sec
Correct option is (b)

81. Correct option is (*)
Integrated rate equation,

$$\frac{1}{a_0 - x} - \frac{1}{a_0} = 2kt$$

$$\frac{a_0-(a_0-x)}{a_0(a_0-x)} = 2kt$$

$$\frac{x}{a_0 - x} = 2a_0kt$$

$$\frac{x}{2(a_0 - x)} = a_0kt$$

Plot of $\frac{x}{2(a_0-x)}$ vs time gives a slope of a_0k.

82. Correct option is (a)

$$[N_2O_2] = \frac{k_1[NO]^2}{k_2[O_2] + k_{-1}} ; \frac{1}{2}\frac{d[NO_2]}{dt} = \frac{k_1k_2[NO]^2}{k_2[O_2] + k_{-1}}$$

$$[O_2] \text{ is in large excess}$$

$$k_2[O_2] \gg k_{-1}; \frac{d[NO_2]}{dt} = \frac{2k_1k_2[NO]^2[O_2]}{k_2[O_2]} = 2k_1[NO]^2$$

83. Correct option is (c)

Energy of one Einstein = $\frac{N_AhC}{\lambda} = \frac{6.02\times10^{23}\times6.6\times10^{-34}\times3\times10^{8}}{600\times10^{-9}} \approx 2\times10^5 J$

Energy of light absorbed by A = $100\times6626\times\frac{50}{100} = 3313005J$

Number of Einstein absorbed = $\frac{331300}{20000} = 1.65$

Moles of B produced are 0.2 so the moles of A decomposed is 0.1 ; $\phi = \frac{0.1}{1.65} = 6 \text{ x } 10^{-2}$

84. Correct option is (c)

For second order kinetics ,k = $\frac{1}{t}\left[\frac{1}{C_t} - \frac{1}{C_0}\right]$

K = $\frac{1}{1}\left[\frac{1}{0.8} - \frac{1}{1}\right] = 0.25 mol^{-1} lit\ min^{-1}; k = \frac{1}{2}\left[\frac{1}{0.67} - \frac{1}{1}\right] = 0.246 mol^{-1} lit\ min^{-1}$

K = $\frac{1}{4}\left[\frac{1}{0.50} - \frac{1}{1}\right] = 0.25 mol^{-1} lit\ min^{-1}; k = \frac{1}{6}\left[\frac{1}{0.40} - \frac{1}{1}\right] = 0.25\ mol^{-1} lit\ min^{-1}$

Data satisfies the second order kinetics

85. Correct option is (b)
from Arrhenius equation

$$\ln\frac{k_2}{k_1} = \frac{E_A}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

$$\ln 2 = \frac{E_A}{8.314}\left[\frac{1}{200} - \frac{1}{300}\right]$$

$E_A = \frac{0.69 \times 8.314 \times 200 \times 300}{100}$ =3441.99 J/mole=3.4 kJ/mole

86. Correct option (a)

This is from Arrhenius concept and according to it,

K=A$e^{-E_a/_{RT}}$

Taking log both sides, we get,

$$logK = logA - \frac{E_a}{2.303RT}$$

given equation is,

$$logK = 14.1 - \frac{10000K}{T}$$

Comparing above equations, we get

$$\frac{E_a}{2.303RT} = \frac{10000K}{T}$$

$$E_a = 10000 \times 2.303 \times 8.314\, J/mol$$

$\Longrightarrow E_a$=191.4 KJ/mol

87. Correct option (b)

When 10% gas is reacted, $[C_1] = [C_o] - 10\%$ of $[C_o] = 0.90[C_o]$

And when 60% gas is reacted, $[C_2] = [C_o]\,] - 40\%$ of $[C_o] = 0.60[C_o]$

Since, $rate \propto [C]^n$

Thus,

$$\Rightarrow \frac{rate_1}{rate_2} = \left(\frac{[C_1]}{[C_2]}\right)^n$$

$$\Rightarrow \frac{10}{5} = \left(\frac{0.9}{0.6}\right)^n$$

$$\Rightarrow 2 = (1.5)^n$$

$$\Rightarrow n \approx 1.71$$

88. Correct option (b)

Dose of compound = 80 $mg.kg^{-1}$

For 70kg person = 80×70 mg = 5600 mg = 5.6 g

Since, $density = \frac{mass}{Volume}$

Thus, $volume = \frac{mass}{density}$

$$\Rightarrow \frac{5.6}{1.45} = 3.86 \approx 3.9\, mL$$

89. Correct option (a)

Since, equilibrium constant $K = \frac{k_1}{k_2}$

Or $k_2 = \frac{k_1}{K} = \frac{3.3\times10^{-4}}{0.16} = 20.68\times10^{-4}\, s^{-1}$

Also, relaxation rate constant $k = k_1 + k_2 = 3.3\times10^{-4} + 20.68\times10^{-4}$

Thus, $k = 23.98\times10^{-4}$

time taken for half the equilibrium amount (half lifetime) is given by;

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{23.98\times10^{-4}} = 289.99 \approx 290s$$

3

Electrochemistry

Hints & solutions

1. Corect option-(c)

For an aqueous solution at298K, the Debye huckel limiting law is-

$\log \gamma_{\pm} = -A| Z_+Z_-|\sqrt{\mu}$

where A=0.509, for aqueous solution at 298K

$\log \gamma_{\pm} = -0.509 \mid Z_+Z_-|\sqrt{\mu}$

2. Correct option-(a)

We have $k = \sqrt{[}\frac{e^2N}{\in(0)\in(r)kT}(\sum c(i)Z(i)^2)]$

$= \sqrt{[}\sum c(i)Z(i)^2] * \frac{1}{(\sqrt{2\in(r)}} * \sqrt{\frac{2e^2N}{\in(0)kT}} = \{\sqrt{[}\sum c(i)Z(i)^2]\frac{1}{\sqrt{2}\in(r)} * 30(nm\sqrt{(}molkg^{-1})^{-1}$

⇨ $k = \frac{\sqrt{0.18}}{10\sqrt{2}} * 30nm^{-1}$

⇨ $k = \frac{9}{10nm^{-1}}$

So debye huckel screening length (κ^{-1})=$\left(\frac{10}{9}\right)$nm.

3. Correct answer (a)

For the oxidation half cell:

Oxidized state(O)+ne$^-$⇌reduced state(R)

From modified Nernst equation (in terms of formal potential E^0)

So, $E = E(0) - \frac{RT}{nF}\ln\left(\frac{[R]}{[O]}\right)$

⇨ $E - E(0) = \frac{RT}{nF}\ln\left(\frac{1}{e^2}\right)$

⇨ $E - E(0) = -\frac{RT}{nF}\ln(e^{-2})$

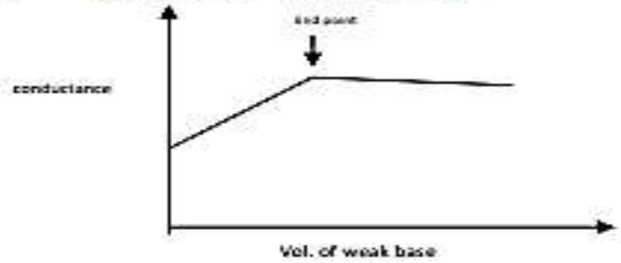
⇨ $E - E(0) = -\frac{(-2)RT}{nF}\,lne$

⇨ $E - E(0) = +\frac{2RT}{nF}$

4. Correct option-(d)

$CH_3COOH + NH_4OH \rightarrow CH_3COO^-(aq) + NH_4^+(aq) + H_2O$

Weak acid weak base ionized salt



When weak base is added to weak acid , then salt is formed which is more dissociated wrt weak acid, so, conductance increases upto end point but after the end point only concentration of weak base increases which remains almost in almost undissociated form so does not lead to increases in conductance.

5. Correct option (c)

In potentiometric titration the rate of change in slope ofE vs V graph has maximum at the equivalence point.

So,$\frac{d}{dV}\left(\frac{dE}{dV}\right) = 0 \; => \frac{d^2E}{dV^2} = 0$

And,as dE/dV can be positive or negative.But, |dE/dV| will be geater than 0.

6. Correct option-(d)

$Fe^{3+}+e \rightarrow Fe^{2+}$;$E_1^o = 0.77V$; $\Delta G_1 = -nFE_1^o = -F\times 0.77$ ….(i)

$Fe^{2+}+2e \rightarrow Fe$; $E_2^o = -0.44V$; $\Delta G_2 = -nFE_2^o = -2F\times(-0.44)$ ….(ii)

Adding the above 2 eqn, we get,

$Fe^{3+}+3e \rightarrow Fe$

$\Delta G_3 = \Delta G_1 + \Delta G_2$

⇨ $-3FE_3^o = -0.77F + 0.88F = 0.11F$

⇨ $E_3^o = \frac{-0.11}{3} = -0.04V.$

7. Let one faraday of electricity is withdrawn from the cell.

(i) Electrode reaction at anode $Ag(s)+Cl^-(a_1) \rightarrow AgCl(s) + e^-$

(ii) Electrode reaction at cathode $AgCl(s)+e^- \rightarrow Ag(s)+Cl^-(a_2)$

(iii) Migration of K^+ ions $t_+K^+(a_1) \rightarrow t_+K^+(a_2)$

(iv) Migration of Cl^- ions $t_-Cl^-(a_2) \rightarrow t_-Cl^-(a_1)$

The net effect is obtained by adding the above four changes, which gives

$Cl^-(a_1)+t_+K^+(a_1)+t_-Cl^-(a_2) \rightarrow Cl^-(a_2)+t_+K^+(a_2)+t_-Cl^-(a_1)$

Therefore,

$t_+K^+(a_1)+t_-Cl^-(a_1) \rightarrow t_+K^+(a_2)+t_-Cl^-(a_2)$

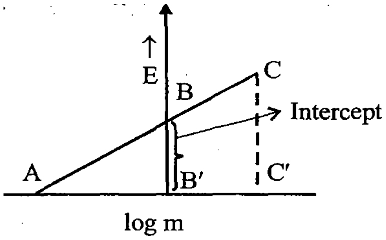
8. $\Lambda^o_{(HCOOH)} = \lambda^o_{(HCOO^-)} + \lambda^o_{(H^+)}$

$$= \Lambda^o_{(HCOONa)} + \lambda^o_{(HCl)} - \left\{\frac{1}{2}\Lambda^o_{(Na_2SO_4)} + \Lambda^o_{(KCl)} - \frac{1}{2}\Lambda^o_{(K_2SO_4)}\right\}$$

$$= 105 + 426 - \left\{\frac{1}{2}(260) + 150 - \frac{1}{2}(308)\right\}$$

= 405 S cm^2 mol^{-1}

9. Correct option(c)
If we take a half cell



$H^+ + e^- = \frac{1}{2} H_2$

$$E = E(0) - \frac{RT}{Nf}\ln\left(\frac{1}{M(H+)}\right)$$

$$E = E(0) + \frac{RT}{Nf}\ln M(H+)$$

Then, E vs logm graph gives intercept E^0 .

intercept given by BB'.

10. Correct option(c)
$E_{CELL}=E_L-E_R=(E_{Cl-|AgCl|Ag}-E_{H+|H2|Pt})_L+(E_{H+|H2|Pt}-E_{Cl-|AgCl|Ag})_R$
Nernst equation for each potential

$$E_{CELL}=[E^0_{Cl-|AgCl|Ag}-(RT/F)\ln(a_{cl-})_1+(RT/F)\ln\frac{(P|P^0)^{\frac{1}{2}}}{(aH+)1}]+[-E^0_{Cl-|AgCl|Ag}+(RT/F)\ln(a_{cl-})_2-\quad(RT/F)\ln\frac{(P|P^0)^{\frac{1}{2}}}{(aH+)2}]$$

$E_{CELL}= (RT/F)\ln\{(a_{H+})_2(a_{Cl-})_2/(a_{H+})_1\ (a_{Cl-})_1\}$

$= 2(RT/F)\ \ln\ [(a_{\pm})_2/(a_{\pm})_1]$

11. Corect answer (a)
Daniel cell consists of two half celss. The half cell on the left contains a zinc metal electrode dipped in $ZnSO_4$ solution. The half cell on the right consists of copper metal electrode ina solution of $CuSO_4$. The half cell joined by a salt bridge.
Oxidation half cell reaction: Zn (s) → Zn^{2+}(aq) +$2e^-$.
Reduction half cell reaction: Cu^{2+}(aq)+$2e^-$→Cu(s)
Net cell reaction: Zn(s)+Cu^{2+}(aq)→ Zn^{2+}+Cu(s)

12. Corect option(c)

Due to kohlraush's law at infinite dilution, when dissociation is complete, each ion makes a definite contribution towards molar conductance of the electrolyte irrespective of the nature of the ion with which it s associated and that the molar conductance at infinite dilution for any electrolyte is given by the sum of the contribution of the two ions. Only hydrochloric acids in water undergo complete dissociation and contribution with equal ion.

13. Correct answer –(b)

$Fe^{3+}+e^{-} \rightarrow Fe^{2+}$ ×2 …..(1)
$Sn^{2+} \rightarrow Sn^{4+}+2e^{-}$ ……(2)
Net reaction: $2Fe^{3+}+2e^{-}+Sn^{2+} \rightarrow 2Fe^{2+}+Sn^{4+}+2e^{-}$
Since we know that at room temperature , equilibrium constant.

$\log k_{eq} = \frac{nE^0}{0.0591} = \frac{nE^0}{0.06}$

$E^0 = E^0_{right} - E^0_{left} = 0.75 - 0.15 = 0.60$

$\log k_{eq} = \frac{2\times0.6}{0.06} = 20$

⇨ $K_{eq} = 10^{20}$.

14. Correct option (c)

From Debye-huckel limiting law, charge density (ρ)$= \frac{-2ne^2\varphi\Psi}{kT}$

According to Poission equation of electrostatics $\left[\nabla^2\Psi = -\frac{4\pi\rho}{\epsilon(r)}\right] = \left[-\frac{4\pi}{\epsilon(r)}\left(-\frac{2ne^2\Psi}{kT}\right)\right]$

$$\nabla^2\Psi = \frac{8\pi e^2\Psi}{\epsilon(r)kT}$$

The equation may be written as $\nabla^2\Psi = k^2 \ where, \left(k^2 = \frac{8\pi e^2\Psi}{kT}\right)$

The solution is equal to $\Psi = \frac{ze}{\in(r)*r} e^{-(kr)} = \frac{ze}{\in(r)} \left(e^{-kr}/r\right)$, the term is total potential in Debye –huckel it means electrical potential.

$\Psi = \frac{ze}{\in(r)*r}[1-kr] = \frac{ze}{\in(r)r} - \frac{zek}{\in(r)} = \frac{ze}{\in(r)r} - \frac{ze}{\in(r)\left(\frac{1}{k}\right)}$

So, $\Psi = \frac{ze}{\in(r)r} - \frac{ze}{\in(r)\left(\frac{1}{k}\right)}$

term1: potential due to the given ion itself
term2: potential on the ion due to its ionic atmosphere.

15. Correct option (b)

$\Lambda(m) = \Lambda^0(m) - b\sqrt{c}$ ….(1)
If the concentration is 4 times increased.
$\Lambda(m) - \Lambda(m') = \Lambda^0(m) - b\sqrt{c} - \Lambda^0(m) - 2b\sqrt{c}$
⇨ $\Lambda(m) - \Lambda(m') = b\sqrt{c}$

16. Correct option(c)

If S and P have ε=0, then titrant shows parallel and after end point goes increasingly wrt to substrate.

17. Corect option-(b)
$O + ne \rightleftharpoons R$

Nernst equation, $E = E^0 - \frac{RT}{nF}\ln\frac{[R]}{[O]}$

$E - E^0 = -\frac{RT}{nF}\ln\frac{[R]}{[O]}$

$\ln\frac{[R]}{[O]} = -\frac{nF}{RT}[E - E^0]$

⇨ $-\ln\frac{[O]}{[R]} = -\frac{nF}{RT}[E - E^0]$

⇨ $\ln\frac{[O]}{[R]} = \frac{nF}{RT}[E - E^0]$

⇨ $\frac{[O]}{[R]} = e^{\frac{nF}{RT}[E - E^0]}$

18. Correct option (b)
In potentiometric titration , end point is observed by observing the jump in potential.

19. Correct option (b)
Anode: $4OH^- \rightarrow 2H_2O + O\uparrow + 4e-$
Cathode : $2H^+ + 2e^- \rightarrow H_2\uparrow$

20. Correct option-(d)
$Zn \rightarrow Zn^{2+} + 2e^-$ (oxidation)
$Cu^{2+} + 2e^- \rightarrow Cu$ (reduction)
$E^0 = 1.07V, E^0 = 0.34V$, $E = E_{right} - E_{left}$
$1.07 = E_{red.pot.right} - E_{red.pot.left}$
⇨ $1.07 = 0.34 - E_{Zn2+|Zn}$
⇨ $1.07 - 0.34 = E_{Zn2+|Zn}$
⇨ $E_{Zn2+|Zn} = 0.73V$

21. Correct option(b)
$Zn + 2Fe^{+3} \rightleftharpoons Zn^{2+} + 2Fe^{+2}$

Nernst equation:

$E_{cell} = E_0 - \frac{0.0591}{2}\log\frac{[Zn^{2+}][Fe^{2+}]^2}{[Fe^{3+}]^2}$

⇨ $E_{cell} = E_0 - \frac{0.0591}{2}\log\frac{[0.01][0.001]^2}{[0.01]^2}$

⇨ $1.71 = E_0 - \frac{0.0591}{2}\log 10^{-4}$

⇨ $1.71 = E_0 - \frac{0.0591}{2}(-4)\log 10^1$

⇨ $1.71 = E_0 + 0.1182$

⇨ $E_0 = 1.5918$

$\Delta G = -RT\ln K_{eq}$

⇨ $-nFE_o = -2.303\times 8.314\times 298\times log\ K_{eq}$

⇨ $-2\times 96500\times 1.5918 = -2.303\times 8.314\times 298\times log\ K_{eq}$

⇨ $logK_{eq} = \frac{307217.4}{5705.8} = 53.84$

⇨ $K_{eq} \approx 10^{54}$

22. Correct option (d)

$\lambda^{\infty}_{NaCl} = \lambda^{\infty}_{Na+} + \lambda^{\infty}_{Cl-}$ …(1)

$\lambda^{\infty}_{NaI} = \lambda^{\infty}_{Na+} + \lambda^{\infty}_{I-}$ …(2)

$\lambda^{\infty}_{RbI} = \lambda^{\infty}_{Rb+} + \lambda^{\infty}_{I-}$ …(3)

add (1) and (3) substract (2)

$\lambda^{\infty}_{Na+} + \lambda^{\infty}_{Cl-} + \lambda^{\infty}_{Rb+} + \lambda^{\infty}_{I-} - \lambda^{\infty}_{Na+} - \lambda^{\infty}_{I-} = 12.7 + 9.1 - 10.8$

$\lambda^{\infty}_{Cl-} + \lambda^{\infty}_{Rb+} = 21.8 - 10.8$

$\lambda^{\infty}_{RbCl} = 11.0$ mS m^2 mol.

23. Correct option-(c)

According to the kohlrausch law of molar conductance strong electrolyte decreases linearly with square root of conc while that of weak electrolyte decreases exponentially . hence, (c) is a strong electrolyte while D is a weak electrolyte.

24. Correct option(b)

Debye Huckel screening lengths-

$\kappa = \sqrt{\frac{e^2NA}{\epsilon(0)\epsilon(r)kT}\left(\sum c(i)Z(i)^2\right)}$

⇨ $\frac{1}{\kappa} = \sqrt{\frac{\epsilon(0)\epsilon(r)kT}{e^2NA(\sum c(i)Z(i)^2)}}$

⇨ $\frac{1}{\kappa} \propto \sqrt{\in(0)}$

So, $\frac{1}{\kappa} \propto \sqrt{4} = 2$

$\frac{1}{\kappa} \propto \sqrt{25} = 5$

$\frac{1}{\kappa} \propto \sqrt{81} = 9$

25. Correct option(b)

(I) cell A and B

A. $Fe(OH)_2$ (s) + $2e^-$ → Fe (s) + $2OH^-$ (aq) ; E^o = –0.877V

B. Al^{+3} (aq) + $3e^-$ → Al (s) ; E^o = 1.66V

$E^o = E_{right}^0 - E_{left}^0$

$= -0.87-(-1.66)=+0.79V$

$\Delta G=-nFE$ (E=+ve)

$\Delta G=-ve$ (spontaneous)

Fe reduced.

(II) A and C

A. $Fe(OH)_2$ (s) + $2e^-$ → Fe (s) + $2OH^-$ (aq) ; E^o = -0.877V

C. AgBr (aq) + e^- → Ag (s) + Br^- (aq) ; E^o = 0.071V

$E^0 = E_{right}^0 - E_{left}^0$

$= 0.071-(-0.087)=0.948V$

$\Delta G=-nFE$ (E=+ve)

$\Delta G=-ve$ (spontaneous)

In this cell Fe carried negative reduction potential goes to left hand side of the half cell and in this half cell oxidation occur. Fe oxidized.

26. Corect option (a)

$E - E^0 = -\frac{RT}{nF} lnQ$ (1)

At eqm. Q=K(equilibrium const) and $E_{cell}=0$.

So, $E^0 = -\frac{RT}{nF} lnK$ (2)

Sn^{4+} (aq) + 2e → Sn^{2+} (aq), E^o = 0.15V

Sn^{2+} (aq) + 2e → Sn (s), E^o = -0.14V

$E^0_{cell} = E^{red}_{cathode} - E^{red}_{anode} = 0.15-(-0.14)=0.29$ V.

Putting value of E^0_{cell} in eq.(2)

$E^0_{cell} = \frac{RT}{nF} lnK$

⇨ $0.29 = \frac{RT}{nF} \ln K$

$N=2RT/F=25.7\times10^{-3}$ V

$0.29 = 25.7\times \frac{0.001}{2} lnK$

$0.29\times \frac{2}{25.7} \times 0.001 = lnK$

$lnK = 22.6$

27. Correct option(b)

$\Delta G=-nFE$ (ΔG=-ve spontaneous)

$\Delta G=2746.06\times10^3$ J/mole

$\Delta G=2746.06\times10^3 = -26\times96500\times E$

⇨ $E = \frac{2746.06*1000}{26*96500} = \frac{2746060}{2509000} = 1.09V$

28. Correct option-(d)

$Zn\ (s) \rightarrow Zn^{+2}\ (aq)\ +\ 2e$
$Cu^{2+}(aq)\ +\ 2e\ \rightarrow Cu\ (s)$
$Cu^{2+}(aq)\ + Zn\ (s) \rightarrow Zn^{+2}\ (aq) + Cu\ (s)$
$\Delta G = \Delta G^0 + RT\ln Q$

$E_{cell} = E^0{}_{cell} - (RT/nF)\log Q$ … (1)

Eq.(1) ×-nF

$-nFE_{cell} = -nFE^0{}_{cell} + RT\ln Q$

$\Delta G = \Delta G_0 + RT\log \frac{[Zn^{2+}][Cu(s)]}{[Cu^{2+}][Zn(s)]} => Q = \frac{[Zn^{2+}]}{[Cu^{2+}]}$

$\Delta G^0 + RT\ \ln\ \left(\frac{a_{Zn^{2+}}}{a_{Cu^{2+}}}\right)$

29. Correct option(b)

$\text{Log}\frac{k}{k_o} = 2AZ(A)Z(B)\sqrt{I}$

GIVEN : $2AZ(A)Z(B)\sqrt{I} = -4\times 0.51\sqrt{I}$

⇨ Z(A)Z(B)=–2

30. Correct option(c)

$\Delta G = -nFE_{cell}$
Gibbs Helmholtz Equation,
$\Delta G = \Delta H + T\left(\frac{\partial(\Delta G)}{\partial T}\right)(P)$ …(1)
$\Delta G = -nFE$
Therefore,we get
$\left(\frac{\partial(\Delta G)}{\partial T}\right) = -nF\left(\frac{\partial F}{\partial T}\right)(P)$ ….(2)
From equatiom(1) and(2),
$-nFE = \Delta H - nFT\left(\frac{\partial E}{\partial T}\right)$ …(3)
Rearranging we have,
$\Delta H = -nF[E - T\left(\frac{\partial E}{\partial T}\right)]$
But, $\Delta G = \Delta H - T\Delta S$ …(4)
⇨ $\Delta S = \left(\frac{\Delta H - \Delta G}{T}\right)$
From eq.(3) and(4),
$-T\Delta S = -nFT\left(\frac{\partial E}{\partial T}\right)$

$\Delta S = nF\left(\frac{\partial E}{\partial T}\right)$

⇨ $\left(\frac{\partial E}{\partial T}\right)(P) = \frac{\Delta S}{nF}$

Temperature dependence$=\frac{\Delta S}{nF}$

31. Correct option (c)

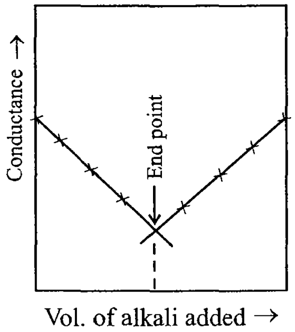
When a strong alkali e.g. sodium hydroxide is added to a solution of a strong acid, e.g. HCl, the reaction:

$(H^+ + Cl^-) + (M^+ + OH^-) \rightarrow M^+ + Cl^- + H_2O$

a) During the reaction highly conducting H^+ are replaced by M^+ which has much lower conductance, so addition of alkali to acid solution is accompanied by decrease of conductance.

b) When neutralization is complete then the further addition of alkali results in an increase of conductance, since the sodium ion and hydroxyl ions are no longer up in the chemical reaction.

c) At the neutral point the conductance of the system will have a minimum value.



32. Correct option(d)

K→ Kohlrausch's constant is specified for uni-valent electrolyte (stoichiometry) and strong electrolyte (specific identity).

33. Correct option(c)

$0.1M\ Na_2SO_4 \rightleftharpoons 2Na^+ + SO_4^{2-}$

$\qquad\qquad\qquad 2\times0.1 \qquad 0.1$

$I = \frac{1}{2}[m(1)z(1)^2 + m(2)z(2)^2] = \frac{1}{2}[0.2 + 0.4] = \frac{1}{2} * 0.6 = 0.3$

$MgSO_4 \rightleftharpoons Mg^{2+} + SO_4^{2-}$

Let conc. m m m

Ionic strength=0.3

$$I = \frac{1}{2}[m(1)z(1)^2 + m(2)z(2)^2]$$

⇨ $I = \frac{1}{2}[m * 4 + m * 4]$

⇨ $0.3 = \frac{8m}{2} => m = \frac{0.6}{8} = 0.075M$

34. Correct option(d)

Reaction1:

$\frac{1}{2} Cl_2 + e^- \rightarrow Cl^-$; $E^0 = 1.35$ V

Reaction 2:

$AgCl \rightleftharpoons Ag^+ + Cl^-$; $E^0 = (0.06/n) \log k_{sp} = 0.06 \log 10^{-10} = -0.6$

Reaction 3:

$Ag^+ + Cl^- \rightleftharpoons AgCl$; $E^0 = 0.6$

On adding reaction (1) and (3) , we get,

$\frac{1}{2} Cl_2 + Ag^+ + e^- \rightarrow AgCl(s)$

$$E_3 = \frac{n(1)E(1)+n(2)E(2)}{n(3)} = \frac{1*1.35+1*0.6}{1} = 1.95\ V$$

35. Correct option(b)

$\frac{1}{2} H_2 \rightarrow H^+(aq) + e^-$

$AgCl + e^- \rightarrow Ag(s) + Cl^-$

Net reaction: $\frac{1}{2} H_2 + AgCl \rightarrow H^+(aq) + Ag(s) + Cl^-(aq)$

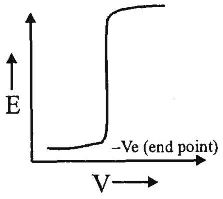
$\Delta S = nF\left(\frac{\partial E}{\partial T}\right)$. As, entropy of reaction decreases because gaseous is being consumed .

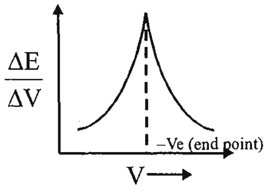
So, $\Delta S < 0$.

$\left(\frac{\partial S}{\partial T}\right) < 0$;E^0_{cell} decreases with increase in temperature.

36. Corect option(b)

At end point, it shows $\frac{dE}{dV} \neq 0\ and\ \frac{d^2E}{dV^2} = 0$



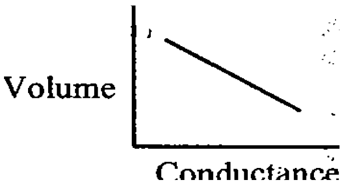


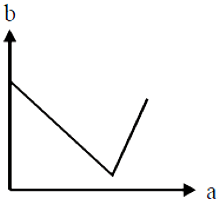
37. Correct option (d)

$NaOH + (HCl + CH_3COOH)$

First NaOH will react with HCl will use NaOH is completely titrated during this process conductance will decrease due to loss of OH^- ions.

Second after than, as NaOH is completely consume. So, simple addition of mixture of HCl and CH_3COOH will only increase the conductance





38. Correct option (d)

The standard electrode potential E_0 at a fixed temperature and in agiven medium is dependant on the electrode reaction ad the electrode composition.

39. Correct option (a)

Debye huckel screening length:

$$\kappa = \sqrt{\frac{e^2NA}{\epsilon(0)\epsilon(r)kT}\left(\sum C_iZ_i{}^2\right)}$$

$$\Rightarrow \quad \frac{1}{\kappa} = \sqrt{\frac{\epsilon(0)\epsilon(r)kT}{e^2NA(\sum c(i)Z(i)^2)}}$$

$$\frac{1}{\kappa(A)} = \sqrt{\frac{T(A)}{C(A)}} \quad \ldots(1)$$

$$\frac{1}{\kappa(B)} = \sqrt{\frac{T(B)}{C(B)}} \quad \ldots(2)$$

$\frac{1}{\kappa(A)} = \frac{1}{\kappa(B)}$ only if,$T_A=2T_B$; $C_A=2C_B$

Putting this value in eqn. (1)

$$\frac{1}{\kappa(A)} = \sqrt{\frac{2T(B)}{2C(B)}} = \sqrt{\frac{T(B)}{C(B)}}$$

$\frac{1}{\kappa(B)} = \sqrt{\frac{T(B)}{C(B)}}$ Fom eqn.(2).

Eq(1)= Eq(2).

40. Correct option (a)

$$t_+ = \frac{u_+}{u_+ + u_-}$$

$$u_+ = 6\times10^{-4} \text{ and } u_- = 5\times10^{-4}$$

$$t_+ = \frac{6\times10^{-4}}{6\times10^{-4} + 5\times10^{-4}} = \frac{6}{11} = 0.545$$

$$t_- = 1 - t_+ = 1 - 0.545 = 0.455$$

41. Correct option (b)

$$AlCl_3 \rightarrow Al^{+3} + 3Cl^{-1}$$

0.008 0 0

0 0.008 0.024

$$KCl \rightarrow K^{+} + Cl^{-1}$$

0.005   0   0

0   0.005   0.005

$$I = \frac{1}{2}\sum C_i {Z_i}^2$$

$$= \frac{1}{2}(0.008(3)^2 + 0.024(1)^2 + 0.005(1)^2 + 0.005(1)^2)$$

$$= 0.053$$

42. Correct option (c)

$$K_{salt} = K_{solution} - K_{water} = (1.5\times10^{-3} - 1.5\times10^{-5})ohm^{-1}dm^{-1}$$

$$K_{salt} = 1.5\times0.99\times10^{-3}$$

Solubility (s) $=\frac{K_{salt}}{\Lambda_{salt}}$

$$s = \frac{(1.5\times0.99\times10^{-3})ohm^{-1}dm^{-1}}{(0.485 + 1)ohm^{-1}dm^2mol^{-1}}$$

$$s = \frac{1.485}{1.485}\times10^{-3}\ mol\ dm^{-3}$$

$$s = 1\times10^{-3}\ mol\ dm^{-3}$$

$$s = 1\times10^{-3}\times200\ gm\ dm^{-3}$$

$s = 2\times10^{-1}\ gm\ L^{-1}$ $(1dm^3 = 1L)$

43. Correct option (c)

$Zn + 4NH_3 \rightarrow Zn(NH_3)_4{}^{2+} + 2e^-$ $E^o = 1.03V$ ………………(1)

$Zn \rightarrow Zn^{2+} + 2e^-$ $E^o = 0.763V$ ……………. (2)

On reversing 2nd reaction and adding to 1st

Anode: $Zn + 4NH_3 \rightarrow Zn(NH_3)_4{}^{2+} + 2e^-$

Cathode: $Zn^{2+} + 2e^- \rightarrow Zn$

$$Zn^{2+} + 4NH_3 \rightarrow Zn(NH_3)_4{}^{2+}$$

Equilibrium constant of above cell reaction is formation constant

$$E^o_{cell} = E^o_{red}{}^{cathode} - E^o_{red}{}^{anode}$$

But values in equation are given in oxidation potential

So, $E^o_{red}{}^{cathode} = -0.763$

$$E^o_{red}{}^{anode} = -1.03$$

$$E^o_{cell} = -0.763 + 1.03$$

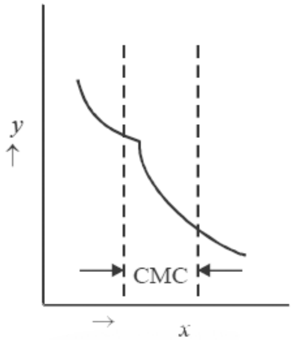
$E^o_{cell} = 0.267$

Now, $E^o_{cell} = \frac{0.0591}{n} logK_{eq} \quad \Rightarrow \frac{0.267\times2}{0.0591} = logK_{eq} \quad \Rightarrow 9.03 = logK_{eq}$

$K_{eq} = 10^{9.03} \qquad \Rightarrow K_{eq} \approx 10^9$

44. Correct option (d)

The molar conductance of anionic surfactant of the type Na^+R^- (sodium dodecylsulfate in water) in water is plotted against the square root of the normality of the solution. The curve obtained, instead of being the smoothly decreasing curve characteristic of ionic electrolytes of this type, has a sharp break in it, at low concentrations. This sharp break in the curve accompanied by reduction in the conductance of the solution, indicating a sharp increase in the mass per unit charge of the material in solution, is interpreted as evidence for the formation of micelles at that point from the unassociated molecules of surfactant with part of the charge of the micelle neutralized by associated counter ions. The concentration at which this phenomenon occurs is called the critical micelle concentration (CMC)



The effect of concentration of electrolyte is given by

$logCMC = -a\ logc_i + b$

For homologous ionic surfactant

$logCMC = A - BN$

45. Correct option (d)

At equilibrium e is zero , because ΔG is zero at equilibrium .

$\Delta G = -nFE$

If $\Delta G = 0$, so, $E=0$.

46. Correct option(b)

$$k = G\times\left(\frac{l}{A}\right)$$

⇨ $0.176 = G\times0.255$

⇨ $G = \frac{0.176}{0.255} = 0.6901\ \Omega^{-1}$.

47. Correct option (c)

$Z + Cu^{2+} \rightleftharpoons Zn^{2+} + Cu$

$E^0 = 1.1$ V

$\Delta G^0 = -nFE^0 = -2\times96500\times1.1 = -212300\ Jmol^{-1} \approx -212\ kJ\ mol^{-1}$

48. Correct option (c)

$Fe^{3+} + e^- \rightarrow Fe^{3+}$

$E_{Fe3+|Fe2+} = E^0_{Fe3+|Fe2+} - \frac{0.0591}{n}\log Q$

$E^0_{Fe3+|Fe2+} = E^0_{Fe3+|Fe2+} - \frac{0.0591}{n}\log\frac{|Fe^{2+}|}{|Fe^{3+}|}$

a) When 50% of Fe^{3+} is titrated

$Fe^{3+} + e^- \rightarrow Fe^{2+}$
x 0
0.5x 0.5x

$E^0_{Fe3+|Fe2+} = E^0_{Fe3+|Fe2+} - \frac{0.0591}{1}\log\frac{0.5x}{|0.5x|}$

⇨ $E^0_{Fe3+|Fe2+} = E^0_{Fe3+|Fe2+} = 0.77$

b) When 80% of Fe^{3+} is titrated

$Fe^{3+} + e^- \rightarrow Fe^{2+}$
x 0
0.2x 0.8x

$E^0_{Fe3+|Fe2+} = E^0_{Fe3+|Fe2+} - \frac{0.0591}{1}\log\frac{0.8x}{|0.2x|}$

⇨ $E^0_{Fe3+|Fe2+} = 0.77 - 0.0591\log 4 = 0.77 - 0.0591\times 2\log2$

⇨ $E^0_{Fe3+|Fe2+} = 0.734$

49. Correct option(a)

$Pt|H_2(g)|HBr(aq)|AgBr(s)|Ag(s)$

$E^0 = 0.01 - 1\times10^{-4}(T-298) - 2\times10^{-6}(T-298)^2$

$\left(\frac{\partial E^0}{\partial T}\right)(P) = -1\times10^{-4} - 2\times2\times10^{-6}(T-298)$

$\left(\frac{\partial E^0}{\partial T}\right)(P) = -10^{-4} - 4\times10^{-6}(T-298)$

$$\Delta S = nF\left(\frac{\partial E}{\partial T}\right)(P) = 2\times96500\{-10^{-4} - 4\times10^{-6}(298-298)\}$$

$$= -193000\times10^{-4}$$

$= -19.3\,JK^{-1} = -\frac{19.3}{2} = -9.65JK^{-1}\,mol^{-1}$

$$\Delta H = -nFE^0 + nFT\left(\frac{\partial E}{\partial T}\right)(P)$$

$$= -9650\times[0.01 - 10^{-4}(298-298) - 2\times10^{6}(298-298)^2 + 298\times(-9.65)]$$

$= -965 - 2875.7$

$= -3840.7Jmol^{-1}$

$= -3.840\,kJmol^{-1}$

50. Correct option (b)

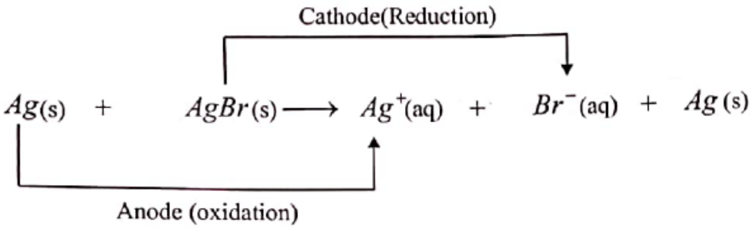
Salt bridge allows flow of current between the two half cells without mixing the solutions. It also completes the circuit and neutralizes excess charged ions. It consists of an electrolyte get and does not affects the rate of reaction.

51. Correct option (c)

The given cell

$AgBr\,(s) \rightarrow Ag^+(aq) + Br^-(aq)$

Can be written as:



$E^o_{cell} = E^o_{Br^-|AgBr|Ag} - E^o_{Ag^+|Ag} = 0.07 - 0.080$

$E^o_{cell} = -0.73V$

$$\Delta G^o = -nFE^o_{cell} = -1\times 96500\times(-0.73) = 70445\,Jmol^{-1} = 70.4\,kJmol^{-1} \approx 70\,kJmol^{-1}$$

52. correct option (a)

$$k_{saturated\ solution} = k_{H_2O} + k_{AB_2}$$

$$k_{AB_2} = 21 - 7 = 14\mu Sm^{-1} = 14\times 10^{-6} Sm^{-1}$$

$AB_2 \rightleftharpoons A^{2+} + 2B^-$

$$\Lambda^o_{(AB_2)} = \lambda^o_{(A^{2+})} + 2\lambda^o_{(B^-)}$$

$$\Lambda^o_{(AB_2)} = 12.72 + (2\times 7.64) = 28mS\,m^2mol^{-1} = 28\times 10^{-3}\,S\,m^2mol^{-1}$$

$$\Lambda^o_{(AB_2)} = \frac{k_{AB_2}}{1000\times S_{AB_2}} \Rightarrow\ S_{AB_2} = \frac{k_{AB_2}}{1000\times \Lambda^o_{(AB_2)}} = \frac{14\times 10^{-6}}{10^3\times 28\times 10^{-3}}$$

$$S_{AB_2} = 0.5\times 10^{-6} \Rightarrow\ S_{AB_2} = 0.5\times 10^{-7}\,molL^{-1} = 5\times \frac{10^{-7}}{10^{-3}}\frac{mol}{m^3} = 5\times 10^{-4}\,mol\,m^{-3}$$

53. Correct option (c)

$$Sn\ +\ Sn^{4+}\ \rightleftharpoons\ Sn^{2+}\ +\ Sn^{2+}$$

Reduction (Cathode)

Oxidation (Anode)

$E^0_{cell} = \frac{RT}{nF}\,lnK_{eq}$

$$\Rightarrow\quad E^o_{Sn^{4+}|Sn^{2+}} - E^o_{Sn^{2+}|Sn} = \frac{2.303\times 8.314\times 300}{2\times 96485}\,logk_{eq}$$

$$\Rightarrow\quad 0.15 - (-0.15) = 0.02976\,logk_{eq}$$

$$\Rightarrow\quad logk_{eq} = 10.08\ \Rightarrow\ k_{eq} = 10^{10.08}$$

54. Correct option (b)

$$\mu = \frac{Ze}{6\pi\eta r}$$

Or, $r = \frac{Ze}{6\pi\eta\mu} = \frac{2\times1.6\times10^{-19}}{6\times3.14\times10^{-3}\times8\times10^{-18}}$ $\{1PaS = 10\, poise = 10^3 cP\}$

$=212.3\times10^{-12}\, m = 212.3\, pm$

55. Correct option (b)
According to Tafel equation

$$\eta_i = \frac{RT}{\alpha F} ln \left(\frac{J_i}{J_o}\right)$$

Now, $\eta_{0.6} = \frac{RT}{\alpha F} ln \left(\frac{J_{0.6}}{J_o}\right)$ and $\eta_{0.5} = \frac{RT}{\alpha F} ln \left(\frac{J_{0.5}}{J_o}\right)$

$$\eta_{0.6} - \eta_{0.5} = \frac{RT}{\alpha F} ln \left(\frac{J_{0.6}}{J_{0.5}}\right)$$

$$\ln\left(\frac{J_{0.6}}{J_{0.5}}\right) = \left(\frac{\alpha F}{RT}\right)(\eta_{0.6} - \eta_{0.5}) = \left(\frac{0.5F}{RT}\right)(0.6 - 0.5) = \left(\frac{0.05F}{RT}\right)$$

56. Correct option (c)
$AgCl + e^- \rightarrow Ag + Cl^-$

$$E = E^0 - \frac{0.0541}{n}\log[Cl^-]$$

$$E = 0.22 - 0.0591 log 10^{-2} = 0.338$$

57. Correct option (d)

In alkaline solution, alkali cation can participate in the conductor resulting in the decrease in transport number of hydrogen ion from 1. Since, potassium ion has the lowest conductor. Therefore, the error is least for 1M KCl.

58. Correct option (a)

$$LJP = (t_- - t_+)\frac{RT}{F} ln \left(\frac{C_2}{C_1}\right)$$

The solution in which the difference between t_- and t_+ is maximum has highest LJP. Since anion is common in all the solutions. Therefore, the difference is divided by transport number of cation in solution, since t_{H^+} is maximum.

Hence, liquid junction potential is maximum where H^+ is used.

59. Correct option (d)

$$k^{-1} = \sqrt{\frac{\in kT}{2e^2 N_A I}} \quad \Rightarrow \quad k^{-1} \propto \frac{1}{\sqrt{I}}$$

Larger the value of $\sqrt{I}$, smaller the value of k^{-1}

$$I_{LaCl_3} > I_{CuCl_2} \approx I_{Na_2SO_4} > I_{NaCl}$$

60. Correct option (a)

Pt| H_2 | H^+ || M^+ | M
(1atm) (1M)

At anode $\frac{1}{2}H_2 \rightarrow H^+ + e^-$ $E^o = 0$

At cathode $M^+ + e^- \rightarrow M$ $E^o_{M^+|M}$

$$M^+ + \frac{1}{2}H_2 \rightarrow M + H^+ \qquad E^o_{cell} = E^o_{M^+|M}$$

$$E_{cell} = E^o_{cell} - \frac{2.303RT}{F} log \frac{[H^+]}{P_{H_2}^{1/2}[M^+]}$$

$$E_{cell} = E^o_{M^+|M} - \frac{2.303RT}{F} \log m$$

Intercept on y-axis will yield $E^o_{M^+|M}$ if a plot between E_{cell} vs. T *log* m is plotted.

61. Correct option is (d)

The solution will contain 0.02 mol kg^{-1} of Na^+ and Cl^-, and 0.03 mol kg^{-1} of Ca^{+2} and 0.06 mol kg^{-1} of NO^{3-}

Ionic strength of the mixture is

$$I = \frac{1}{2}[0.02(1)^2 + 0.02(1)^2 + 0.03(2)^2 + 0.06(1)^2]$$

$$= \frac{1}{2}[0.02 + 0.02 + 0.12 + 0.06] = 0.11$$

$$log\,\gamma_{\pm} = -0.509|1\times1\times2\times1|\sqrt{0.11} \quad \Rightarrow \; log\,\gamma_{\pm} = -\sqrt{0.11}$$

62. The Enthalpy change (ΔH) is given as,

$$\Delta H = \; \Delta G + T\Delta S \; = -nFE^{\circ}_{Cell} + nF\left(\frac{dE^{\circ}_{Cell}}{dT}\right)\times \mathrm{T}$$

substituting values from the question, we get

$$\Delta H = -2\times96500\times0.675 + 2\times96500\times-6.5\times10^{-4}\times300$$

$$\Delta H = -130275 - 37635$$

$$\Delta H = -167910\,Jmol^{-1} \approx 168\,kJmol^{-1}$$

63. correct answer is (b).

This is a direct equation of Ostwald's dilution law

$$\frac{1}{\lambda} = \frac{1}{\lambda^o} + \frac{C\lambda}{K\lambda^o}$$

64. Correct option (a)

$$KNO_3 \leftrightharpoons K^+ + NO_3^-$$

	KNO_3	K^+	NO_3^-
t=0	0.11	0	0
at t	0	0.11	0.11

similarly,

$$Ba(NO_3)_2 \leftrightharpoons Ba^{2+} + 2NO_3^-$$

	$Ba(NO_3)_2$	Ba^{2+}	$2NO_3^-$
t=0	c	0	0
at t	0	c	2c

Since Ionic Strength = $\frac{1}{2}\sum c_i z_i^2$

Thus total ionic strength = 1 = $\frac{1}{2}(0.11\times(+1)^2 + 0.11\times(-1)^2) + \frac{1}{2}(c\times(+2)^2 + 2c\times(-1)^2)$

$$\Rightarrow \frac{1}{2}(0.22 + 6c) = 1$$

$$\Rightarrow 6c = 1.78$$

$$\Rightarrow c = \frac{1.78}{6} = 0.297\,mol.kg^{-1}$$

Since for 1kg we get 0.297 mol

For 500 g, we get, $\frac{0.297}{2}$ = 0.148 mol

Thus, amount of Ba(NO_3)$_2$ required to be added = $0.148 \times 261.32 = 38.76 \ \approx 38.8\ g$

65. **Correct option (c)**

Buffer solutions containing ammonia and an ammonium salt have been widely used as supporting electrolytes in polarographic analysis.

Gelatin is added to the polarographic measurement to reduce the streaming motion of falling mercury drops.

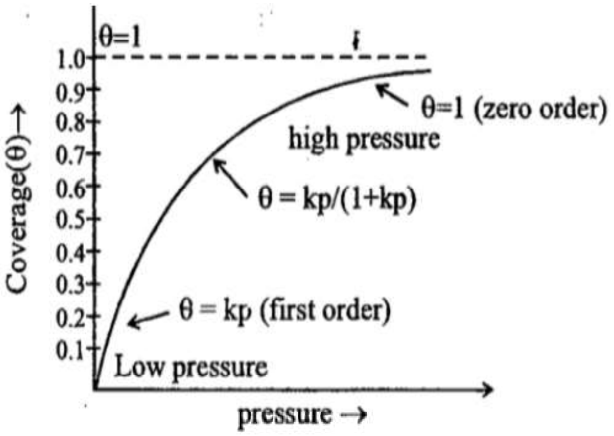
The term depolarization refers to a process that enables current to pass through the cell. Substances taking part in electrochemical reactions are called depolarizers because their presence causes the passage of current when the applied potential is sufficiently large.

Surface Chemistry

Hints & Solutions

1. Correct answer: (a)

For Langmuir adsoption (Monolayer, only)



$$\theta = \frac{kp}{1+kp}$$

At lower pressure , kp << 1

So, that θ = Kp $\Rightarrow$ $\theta \propto p$

At hight pressure, kp >> 1

θ = 1 (Independent of p)

As Langmuir assumed that binding at a site has no influence on the properties of neighbouring sites; this means that enthalpy of adsorption is independent of coverage.

QUANTA POINT

2. **Correct answer: (b)**
In Langmuir isotherm, Fractional coverage (θ)= $\frac{Kp}{1+Kp}$

Case 1: At low pressure, kp << 1

$\theta =$ kp (directly proportional to pressure)

Case II: At high pressure, kp >> 1

0=kp/kp =1 (Independent of pressure)

3. **Correct answer is (c).**
If charge on cation is high then its flocculation value will be low for an anionic sol and if charge on anionic sol is high then its flocculation value will be low for a cationic Sol. As K_2SO_4 has low flocculation value than KBr (due to SO_4^{2-} has higher are charge than Br^-); so sol. A is cationic in nature. On sol B, $CaCl_2$ has low flocculation value than NaCl due to higher the change on calcium ion than sodium ion. So sol B is negatively charged.

4. **Correct option (d)**
dissociative adsorption ,

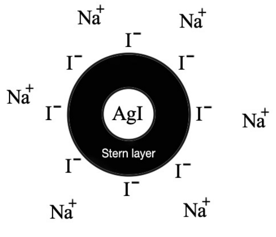
$$\theta = \frac{(KP)^{1/2}}{1+(KP)^{1/2}}$$

5. **Correct answer is (b)**
Dispersion of a solid in a liquid → Sol

Dispersion of a liquid in a gas → Aerosol

Dispersion of a liquid in a liquid → Emulsion.

6. **Correct answer is (a)**
A dilute solution of silver nitrate is add a slight excess of a dilute solution of sodium iodide, a negatively charged solution of silver iodide is formed. This is due to the adsorption of iodide ions.



This is the electrical property of colloid based on t concept of electrical double layer

$AgNO_3 + NaI \rightarrow AgI\downarrow + NaNO_3$

The ions preferentially adsorbed on the surface of a particle of a colloidal system are called potential determining ions. The negatively charged surface of AgI particle attracts the positive ions (Na^+) and repels the negative ions (NO_3^{-1}). The positive Na^+ ions tend to form a compact layer in the vicinity of the potential determining I^- -ion layer. This is called stern layer. The ion present in the stern layer are called counter ions.

7. **Correct answer is (b)**
The molar conductance of anionic surfactant of the type $Na^+ R^-$ in water is plotted against the square root of the normality of the solution. The curve obtained, instead of being the smoothly decreasing curve characteristic of ionic electrolytes of this type, has a sharp break in it, at low concentrations. This sharp break in the curve accompanied by reduction in the conductance of the solution, indicating a sharp increase in the mass per unit charge of the material in solution, is interpreted as evidence for the formation of micelles at that point from the unassociated molecules of surfactant with part of the charge of the micelle neutralized by associated counter ions. The concentration at which this phenomenon occurs is called the critical micelle concentration (CMC)

The effect of concentration of electrolyte is given by

[$\log CMC = -a \log c_i + b$]

For homologous ionic surfactant

[$\log CMC = A - BN$]

8. **Correct answer is (b).**
Langmuir isotherm is given as

$(\theta) = \frac{Kp}{1+Kp} \Rightarrow \theta + \theta kP = KP \Rightarrow \theta = kP(1-\theta) \Rightarrow kP = \frac{\theta}{1-\theta}$

$P = \frac{1}{k}\left(\frac{\theta}{1-\theta}\right) = \frac{1}{0.9}\left[\frac{0.95}{1-0.95}\right] = 21.1$

9. **Correct answer is (a).**
The aggregation of surfactant molecules is defined as micelles.

10. **Correct answer is (b)**
With reference to bulk colloid are thermdonynamically unstable but kinetically stable because inter facial surface tension form thermodynamically unstatle colloid and kinetically stable colloid formed on electrical double layer.

11. **Correct option is (d)**
When we plot θ vs P Graph it is increasing gradually and multilayered is formed . No monolayer is formed

12. **Correct option is (b)**
13. **Correct answer is (d)**

Diffusion coefficient D = μkT/ez

which measures the mobility of the ion due to its thermal energy. Diffusion is the process which involves the migration of a component in solution which involves the migration of a component its own concentration. Diffusion coefficient in water of sucrose is smallest because its mobility is very low. It contains high concentration of ion. So, migration of component in solution very small.

14. Correct option is (a)

$(\theta)=\frac{Kp}{1+Kp} \Rightarrow \theta + \theta kP = KP \ \Rightarrow \theta = kP(1-\theta) \Rightarrow kP = \frac{\theta}{1-\theta}$

P $=\frac{1}{k}\left(\frac{\theta}{1-\theta}\right) = \frac{1}{30}\left[\frac{0.6}{1-0.6}\right] = 0.05$

15. Correct answer is (c)

The fractional coverage for dissociative adsorption is

$$\theta = \frac{(kp)^{\frac{1}{2}}}{1+(kp)^{\frac{1}{2}}}$$

If P is small, then $\theta = (kp)^{\frac{1}{2}}$

$$\theta \propto p^{\frac{1}{2}}$$

16. Correct option (c)

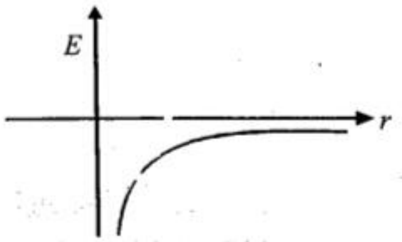
$$\theta = \frac{(kp)^{\frac{1}{2}}}{1+(kp)^{\frac{1}{2}}}$$

$At\ low\ P, 1 \gg (kP)^{\frac{1}{2}}$

$\theta \propto [H_2]^{1/2}$

17. Correct option (a)

The attractive energy due to vander walls interaction is inversely propotional to the sixth power of the interatomic distance . i.e $G_a = \frac{-\beta}{r^6}$



18. Correct option is (a)

Stability of lyophobic dispersions is determined by inter-particle electric double layer repulsion and intra-particle vander waals attraction

19. **Correct option is (d)**

$$\frac{1}{\theta} = \left(\frac{1}{k}\right)\frac{1}{p} + 1$$

Slope = $\frac{1}{k}$

Greater the slope , lesser will be the θ

Therefore , for A will be least

20. **Correct option is (b)**

Total surface area = number of molecules $\times Area$ covered by 1 mole (Ai)

$100\text{cm}^2 = \frac{10^{-5}}{602.3} \times 6.023 \times 10^{23} \times A_i$

$100\text{cm}^2 \times 10^{-10} = Ai$

Ai = 100 Å^2

21. **Correct option is (c)**

In equation [n] = KM^a

[n] represent intrinsic viscocity

22. **Correct option is (c)**

Many properties of nano particles are significantly different different than the corresponding bulk material because large ratio of surface area to volume of nano particles in compare to bulk .

23. **Correct option (b)**

When river water containing colloidal clay flows into the sea . the salt water induces flocculation and coagulation , and is a major cause of silting in estuaries.

24. **Correct option is (c)**

Intermediate colours been understood and correlated to the formation of intermediate nanostructures before the formation of the final gold nanoparticles. Specifically. TEM images have shown that after few seconds of citrate addition, gold nanowires 5 to 8 nm are formed, which are responsible for the dark purple colour. Beyond a certain threshold, the nanowires disintegrate into nanoparticles, and the solution turns ruby-blue.

25. **Correct option is (b)**

K= $\frac{\theta}{1-\theta} \times \frac{1}{P} = \frac{0.1}{1-0.1} \times \frac{1}{25} = 0.004$

26. **Correct option is (b)**

The above critical Micelle concentration, the aggregation of molecules takes place to form Micelle resulting in the drastic decrease in molar conductivity. The size of aggregation is still in colloidal range.

27. Correct option (a)

The height of the column at equilibrium is given by

h=$\frac{2\gamma}{\rho g r}$; $\rho = 1.1\ \frac{gm}{cm^3} = 1.1\times10^3\frac{kg}{m^3}\ , h = 5.0\times10^{-2}m\ , r = 0.2\ \times10^{-3}m$

$\gamma = \frac{\rho g h r}{2} = \frac{1.1\times10^3\times9.8\times5\times10^{-2}\times0.2\times10^{-3}}{2}$

$\gamma = 0.053\ Nm^{-1}$

28. Correct option is (b)

$$\theta = \frac{kP}{1+\ \text{kP}}$$

At very low pressure, Kp << 1; θ = kP (first order)

At very high pressure kP>>1; θ =1 (zero order)

29. Correct option is (d)

In chemisorption, the force of attraction between adsorbent and adsorbate are of chemical nature and highly specific. Chemisorption forms monolayer and Langmuir adsorption isotherm are applicable.

30. Correct option is (d)

(θ)= $\frac{Kp}{1+Kp}$; 0.5= $\frac{K.1}{1+K.1}$, $k = 1$; (θ)= $\frac{Kp}{1+Kp}$ = $\frac{3.1}{1+3.1}\ \frac{3}{4} = 0.75$

31. Correct option is: (a)

Soaps and Detergents are common example of surfactants.

Soap molecules consists of long chains of alkyl groups which are hydrophobic. When they are added to water, they cause water molecule to spread apart and causing their interaction to be minimal. Hence the surface where these surfactants are present is not that strong now. Thus, it causes a loss of surface tension.

32. Correct option (b)

Since, 1 mol = 22.4 litre (at STP)

And 1 litre = 10^3 cm^3

Thus, 1 mol = 22.4 × 10^3 cm^3

According to question, we have 22.4 $cm^3\ g^{-1}$ of nitrogen gas,

Number of moles of Nitrogen gas = $\frac{22.4}{22.4 \times 10^3} = 10^{-3}$ mol g^{-1}

Surface Area = Number of moles × Avogadro Number × Area occupied by one nitrogen molecule (in cm^2)

$= 10^{-3} \times 6.023{\times}10^{23} \times 16.2 \times (10^{-8})^2\ \ cm^2\ g^{-1}$

$= 9.8 \times 10^8$

33. Correct option (d)

For complete coverage let "m" mg of gas.

$$\theta = \frac{KP}{1+KP} = \frac{x}{m}$$

on rearranging, we get

$$\frac{m}{x} = \left(\frac{1}{K}\right)\left(\frac{1}{P}\right) + 1$$

where m/x represents y coordinates, 1/p represents x coordinates and slope is 1/K

according to question,

x	p
0.25	50
0.2	20

Or

m/x	1/p
m/0.25	1/50
m/0.2	1/20

On solving

m/x	p
4m	0.02
5m	0.05

Using formula for slope = $\frac{y_2-y_1}{x_2-x_1}$

Putting the values, we get, $\frac{5m-4m}{0.05-0.02} = \frac{m}{0.03}$

Comparing with value of slope, $\frac{1}{K} = \frac{m}{0.03}$

Thus, $K = \frac{0.03}{m}$

Now using equation

$$\frac{KP}{1+KP} = \frac{x}{m}$$

and putting x = 0.25, P = 50 bar and $K = \frac{0.03}{m}$

we will get $m = 0.3\ mg$

Thus surface coverage at 50 bar pressure will be

$$\frac{x}{m}\times 100 = \frac{0.25}{0.3}\times 100 = 83\%$$

34. Correct option (c)

According to Jurin's law, height of capillary is given by,

$$h = \frac{2\gamma cos\theta}{\rho gr}$$

where, γ is surface tension, θ is contact angle, ρ is density of liquid, g is acceleration due to gravity and r is radius of the tube.

So we can say,

$$h \propto \frac{\gamma}{\rho}$$

according to question,

$$\gamma_A = \frac{1}{2}\gamma_B$$

$$\rho_A = 2\rho_B$$

thus,

$$h_A = \frac{1}{4}h_B$$

or,

$$h_B = 4\times h_A$$

$$h_B = 4\times 10\text{cm} = 40\text{ cm}$$

5

Nuclear Chemistry

Hints & Solutions

1. Correct answer : (d)

$^{235}_{92}U + ^{1}_{0}n \rightarrow ^{142}_{56}B\alpha + ^{91}_{36}Kr + 3^{1}_{0}n$

Energy released per atom (E) = (Δ m) $c^{2.}$

E = [(235.0435+1.00866)-(141x9164+90.9234+3 $\times$ 1.00866)] $\times$ 1.67 $\times$ 10^{-27} $(3 \times 10^{8})^{2}$J

Therefore, E (per atom) = 2.8x10^{-11} [1 amu-1.67 $\times$ 10^{-27}Kg,c =3x10^{8} m/s]

Energy released from 1 mole disintegration of $^{235}_{92}U$ = E (Per mole)

= E(Peratom)x N_A =2.8x10^{11} x6.023x10^{23}

= 1.68 $\times 10^{13}$ J = 1.68 $\times$ 10^{10} KJ

QUANTA POINT

2. Correct answer: (a)

Saturation factor in neutron activation analysis .

Activity equation A = N$\sigma\psi[1-e^{(-\lambda t_{irr})}]$

$\left[1-e^{(-\lambda t_{irr})}\right]$ = Saturation factor

Saturation factor= $\frac{A}{\psi\sigma N}$, where (A= induced radioactivity , ψ =neutron flux , σ = effective nuclear cross section , N = no. of target atoms , λ = decay constant)

3. Correct answer: (d)

Units 1MeV= 10^6 eV, 1MW= 10^6W, 1 eV=$1.6\times10^{-19}J$

One ^{235}U = 200MeV energy released

= $2\times10^{8}\ eV$ energy released

n = $\frac{N}{N_A} = \frac{W}{M} \Rightarrow N = \frac{W}{M}\times N_a = 1000g \times 6.022\times10^{23}$

$N = 2.56\times 10^{24}\ atoms$

One atom of ^{35}U = $2\times10^{8}\ eV$ energy released

$2.56\times 10^{24}\ atoms$ of ^{235}U = $2.56\times 10^{24}\times2\times10^{8}\ eV\ energy\ released$

= 5.12×10^{23}

P (POWER) = $\frac{Energy\ released}{time} = \frac{5.12\times10^{32}}{24\times60\times60s} = 5.926\times10^{27}eVs^{-1}$

= $5.926\times1.6\times10^{-19}\times10^{27}Js^{-1} = 9.481\times10^{8}W = 9.481\times10^{8}\times10^{-6}$MW $= 948.16MW$

4. Correct option (d)

Penetrating power of γ rays is highest, as the particle is neutral and lightest, followed by β rays and then α rays.

$$ionizing\ power\ (I) \propto mass\ of\ the\ particle$$

order of mass of particle $\alpha > \beta > \gamma$

thus ionizing power will follow the order $l_\alpha > l_\beta > l_\gamma$

5. Correct option (d)

According to Harpoon Mechanism, we have,

$$\frac{e^2}{4\pi\varepsilon_o R} = Ionization\ Energy$$

thus we can say,

$$\Delta E \propto \frac{1}{R}$$

Among the given metals, lowest Ionization Energy is for Rb, thus it should have highest cross section (R)

6

Polymer Chemistry

Hints & Solutions

1. Correct answers is (c)

Method	Polymer Mass
(1) Osmometry (number dependent)	$\overline{M}_n$
(2) Light scattering (weight dependent)	$\overline{M}_w$
(3) Sedimentation (viscocity dependent)	$\overline{M}_z$

2. Correct answers is (b)

Osmotic pressure ,

Where C1 = concentration fo polymer in Mol L-1 unit and B = constant . When concentration is expressed in terms of ‘c’ (gL^{-1}) then , C_1 =Mc

$$\pi = MRTc\ (1+MBc+...) \Rightarrow \frac{\pi}{c} = MRT + BM^2RTc+...$$

$\frac{\pi}{c}$ Vs C graph will give intercept (c’) = MRT

$$M = \frac{C1}{RT}$$

3. Correct answers is (a)

$$\text{Kinetic chain length} = \frac{\text{rate of propagation}}{\text{rate of initiation}}$$

$$= \frac{\text{rate of reaction}}{Ki[I]} = \frac{4\times10^{-3}\,moldm^{-3}s^{-1}}{\left(2\times10^{-3}s^{-1}\right)\left(10-3moldm^{-3}\right)} = 2000$$

4. Correct answers is (c)

We know that,

$$\overline{Mn} = \frac{\sum N_iM_i}{\sum N_i} = \frac{10\times1000+50\times2000+40\times4000}{10+50+40} = 2700$$

$$\overline{Mn} = \frac{\sum N_iM_i^2}{\sum N_iM_i} = \frac{N_1M_1^2+N_1M_2^2+N_3M_3^2}{N_1M_1+N_2M_2+N_3M_3}$$

$$\frac{10\times(1000)^2+50\times(2000)^2+40\times(4000)^2}{10\times1000+50\times2000+40\times4000} = \frac{85\times10^7}{270000}\ ,\qquad P.D.I = \frac{\overline{Mm}}{\overline{Mn}} = \frac{850}{729}$$

QUANTA POINT

(1) Osmometry (number dependent) $\overline{M}_n$

(2) Light scattering (weight dependent) $\overline{M}_w$

(3) Sedimentation (viscocity dependent) $\overline{M}_z$

2. Correct answer is (b).

Osmotic pressure, $\pi = C_1RT\,(1+ BC_1 + ...)$

Where C_1 = concentration of polymer in mol L^{-1} unit and B = constant. When concentration is expressed in terms of 'c' (gL^{-1}) then, $C_1 = Mc$

$\pi = MRTc(1+MBc+...) \Rightarrow \frac{\pi}{c} = MRT+BM^2RTc+...$

$\frac{\pi}{c}$ Vs c graph will give intercept (c')= MRT

$M = \frac{c'}{RT}$

3. Correct answer is (a).

$$kinetic\ chain\ length = \frac{\text{rate of propagation}}{rate\ of\ initiation}$$

$$= \frac{\text{rate of reaction}}{k_i[I]} = \frac{4\times10^{-3}moldm^{-3}s^{-1}}{(2\times10^{-3}s^{-1})(10^{-3}moldm^{-3})} = 2000$$

4. Correct answer is (c)

We know that,

$$\overline{Mn} = \frac{\sum N_iM_i}{\sum N_i} = \frac{10\times1000+50\times2000+40\times4000}{10+50+40} = 2700$$

$$\overline{Mm} = \frac{\sum N_iM_i^2}{\sum N_iM_i} = \frac{N_1M_1^2 + N_2M_2^2 + N_3M_3^2}{N_1M_1 + N_2M_2 + N_3M_3}$$

$$\frac{10\times(1000)^2 + 50\times(2000)^2 + 40\times(4000)^2}{10\times1000 + 50\times2000 + 40\times4000} = \frac{85\times10^7}{270000}$$

$$P.D.I = \frac{\overline{Mm}}{\overline{Mn}} = \frac{850}{729}$$

5. Correct answer is (b)

In the addition polymerization, the reaction proceeds via Free-radical chain reaction.

6. Correct answer is (b)

7. Correct answer is (a)

Kinetic chain length describes the number of chain propagation steps in between the chain initiation step and the chain termination step. Mathematically it is defined as

$$kinetic\ chain\ length = \frac{\text{rate of propagation}}{rate\ of\ initiation}$$

8. Correct answer is (c)

$\mathrm{Kt} = \frac{1}{a-x} - \frac{1}{a}$

Or, $\mathrm{kt} = \frac{1}{[A]_0-x} - \frac{1}{[A_0]}$

$$\frac{1}{[A]_0 - x} = \mathrm{kt} + \frac{1}{[A]_0} = \frac{k[A]_0 + 1}{[A]_0}$$

$$\frac{[A]_0}{kt[A]_0 + 1} = [A]_0 - x$$

$\mathrm{X} = [A]_0 - \frac{[A]_0}{kt[A]_0+1}$

$[A]_0\left[1 - \frac{1}{kt[A]_0+1}\right] = [A]_0\left[\frac{kt[A]_0+1-1}{kt[A]_0+1}\right] = [A]_0\left[\frac{kt[A]_0}{kt[A]_0+1}\right]$

$$\text{the fraction of groups condensed} = \frac{x}{[A]_0} = \left[\frac{kt[A]_0}{kt[A]_0 + 1}\right]$$

9. Correct answer is (b)

Number average molecular weight is determined by osmometry.

10. Correct answer is (a)

Variance = (Difference between molar mass and weight molar mass) ×molar mass

= (16-3)× 13 = 3×13=39

Here molar mass represented x_i and weighted molar mass f_i . In this question data set and there frequency is not given. All the final values are given. So, variance = $\sum \sqrt{E(x^2) - E(x)}$

11. Correct option (b)

A = Monolayer

B = Multilayer without condensation

C = Multilayer with capillary condensation

Therefore, correct answer is (b)

12. Correct answer is (c)

The empirical constants ‘K’ and ‘a’ depends on polymer-solvent pair.

13. Correct option is (d)

Lyophobic colloids are thermodynamically unstable but they are kinetically stable does or does not occur depend on the balance of attractive and repulsive force. For stabilisation to occur, the repulsive forces must dominate.

14. Correct option is (c)

$K_{av} = \frac{1}{1-p} \Rightarrow p = 1 - \frac{1}{k_{av}}$

$\Rightarrow$ p= $1 - \frac{1}{10} = 0.9$

$\Rightarrow$ p= $1 - \frac{1}{50} = 1 - 0.02 = 0.98$

$\Rightarrow$ p= $1 - \frac{1}{100} = 1 - 0.01 = 0.99$

15. Correct option is (c)

Kp = $\frac{\theta}{1-\theta} \Rightarrow kp - kp\theta = \theta$

Kp= $\theta(1 + kp) \Rightarrow \theta = \frac{kp}{1+kp}$

16. Correct option is (b)

$\overline{M_n} \times \overline{M_w} = \frac{\sum N_i M_i}{N} \times \frac{\sum N_i {M_i}^2}{\sum N_i M_i} = N^{-1} \sum_i N_i M_i^2$

17. Correct option is (d)

Average end-to-end distance= $\sqrt{N} = \sqrt{10^6} = 10^3$

18. Correct option is (d)

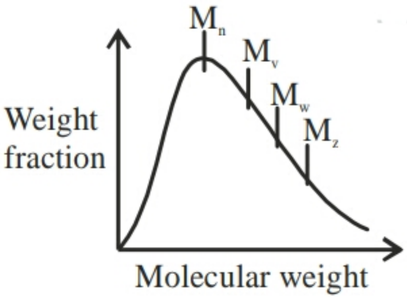
In the FlorySchulz distribution

$P_k = Mo(1-p)^2 p^{k-1}$

Therefore , mole fraction of polymer with a chain length k is

$y_k = \frac{P_K}{M} = \frac{Mo(1-p)^2 p^{k-1}}{Mo(1-p)} = p^{k-1}(1-p)$

19. Correct option is (b)



Correct order is $M_n < M_v < M_w < M_z$

20. Correct option is (b)

P.D.I = $\frac{M_w}{M_n}$ = 1 (for monodisperse)

$\overline{M}_w = \overline{M}_N$

21. Correct option is (b)

$$\overline{M}_n = \frac{10\times20000 + 15\times10000}{10 + 15} = 14000$$

22. Correct option (b)

$$\overline{M_n} = \frac{N_1M_1 + N_2M_2}{N_1 + N_2} = \frac{50\times500 + 75\times6000}{50 + 75} = 5600$$

23. Correct option is (c)

$$\pi = \frac{\mathrm{cRT}}{\mathrm{M}} = \frac{5\times10^3\mathrm{gL}^{-1}\times0.084\mathrm{Latmk}^{-1}\mathrm{mol}^{-1}}{25\mathrm{kgmol}^{-1}} = 0.005$$

24. Correct option (a)

The polydispersity can be expressed in terms of the normalized standard deviation .

Therefore polydispersity= $\frac{\langle M^2\rangle}{\langle M\rangle^2}$

25. Correct option (a)

Contour = $\mathrm{N}\times l = 1000\times150\times10^{-3}\,nm = 150\,nm$

Root mean square length (in nm) = $\sqrt{N}\times l = \sqrt{1000}\times150\times 10^{-3}\,nm = 4.74nm$

26. Correct option is (a)

For a polymer of type A-B-A-B-A-B--A-B.

Let 'P' be the probability that group B combines with group A. For "k' units in the polymer, there are (k-1) linkages between A and B. So, its probability is p^{k-1} .

Probability that group B is not combined with group A be "1-p"

So, for the molecule to terminate after (k-1) linkages, the probability is p^{k-1} (1-p). Similarly, probability that the chain has 'k' units is

N_k/N , where N_k : Number of chains having 'k' units

and N: Total number of chains.

p^{k-1} (1-p) = $\frac{N_k}{N} \Rightarrow \frac{p^k(1-p).}{p} = \frac{N_k}{N}$

Average value of k. $\langle k\rangle = \frac{\sum_{k=1}^{\infty} kN_k}{N}$ or $\langle k\rangle$= (1-p)$\sum_{k=1}^{\infty} kp^{k-1}$

Now , $\sum_{k=1}^{\infty} p^k = 1 + p + p^2 + \cdots = \frac{1}{1-p}$

On differentiating, $\sum_{k=1}^{\infty} kp^{k-1} = (1-p)^{-2}$

Substituting in equation (i), we get

$$\langle k\rangle = \frac{1-p}{(1-p)^2} = \frac{1}{1-p}$$

27. Correct option is (c)

For lllrd order reaction $\frac{1}{[A^2]} - \frac{1}{[A]_0^2} = 2Kt$

Or $\frac{1}{[M^2]} - \frac{1}{[M]_0^2} = 2Kt$

At time t, [M]=[M]$_0$ -x

=[M]$_0$ = [M]$_0$ P= (1-P)[M]$_0$

$\frac{1}{(1-P)^2[M]_0^2} - \frac{1}{[M]_0^2} = 2Kt$

(where P is the fraction of initial concentration) of monomer undergo in polymerisation)

$\frac{1}{(1-P)^2} - 1 = 2K[M]_0^2 t \Rightarrow \frac{1}{(1-P)^2} = 2K[M]_0^2 t + 1$

$\langle N\rangle^2 = 2[M]_0^2$ kt + 1 $\left\{\langle N\rangle = \frac{1}{1-p}\right\}$

28. Correct option is (a)

Root mean square length=$N^{1/2}$ where N is the number of monomer units.

29. Correct option (a)

Rate = $k_2[A]^2 = 3\times10^2\times50\times10^{-3} = 150\times10^{-5} = 1.5\times10^{-3}$

Rate = $\frac{Amount\ of\ monomer\ polymerised}{Time\ taken}$= 1.5×10^{-3}

Amount of monomer polymerized = $1.5\times10^{-3}\times10\times3600 = 54$

30. Correct option is (c)

$[\eta] = \mathrm{K}\overline{M}_V^a$

$0.05 = 5 \times 10^{-5}\overline{M}_V^a \Rightarrow \overline{M}_V^a = \frac{0.05}{5\times10^{-5}}$

$\overline{M}_V^a = 10^3 \Rightarrow \mathrm{M} = 10^6$ gmol^{-1}

31. Correct option (a)

S.No	**Weight fraction (w_i)**	**Molecular weight (m_i)**
1	0.20	10000
2	0.50	40000
3	0.30	60000

Weight average molecular mass = $\sum w_i\, m_i$

$= 0.20\times10000 + 0.50\times40000 + 0.30\times60000$

$= 2000 + 20000 + 18000$

$= 40000$

7

Thermodynamics

Hints & Solutions

1. CORRECT OPTION (c)

From Claussius inequality , ds $ds \geq dq / T$

or, ds-(dq/T) $\geq$ 0 .... (1)

At const. vol, dW =-pdV=0

So, from the first law of thermodynamics,

Dq=du-dw;dq=du. (as, dw = 0)

At const. entropy, dS=0,

From eq.(1) , we get

-(dU)s.v/T $\geq$ 0

Or, (dU)s,v $\leq$ 0

Here, equality holds for reversible process,

So, for spontaneous process,

(dU)s,v < 0

Or, $\Delta U_{s,v} < 0$.

2. CORRECT OPTION (c)

We have, lnk = const $-\left(\frac{\Delta H}{RT}\right)$..... (1)

Given : lnk = 3 + $\frac{2*10^4}{T}$ ....(2)

$$\Delta H^0 = \left(2*10^4*R\right) = -\frac{166KJ}{mol}$$

In eq.(2), multiplying both sides by (-RT),

-RTlink = - 3RT - 2* 10^4 * R .... (3)

$$\Delta G^0 = -T\Delta S^0 + \Delta H^0$$

From eq. (3) and (4)

ΔS^0 = 3R = 24.9 JK^{-1} mol^{-1}

3. CORRECT OPTION (c)

QUANTA POINT

$\mu_1 = \mu_1^0 + RTlnP_1$ (Standard state for component 1 is defined at,
$P_1 = 1\ bar$ (standard pressure)
So, $\mu_1 = \mu_1^0 + R(298)ln1$

- ⇨ $\mu_1 = \mu_1^0$
- ⇨ μ_1^0 is independent pressure but depends on temperature.

4. CORRECT OPTION (B)

$$dU = TdS - PdV \Rightarrow \left(\frac{\partial U}{\partial V}\right)_S = -P$$

⇨

$-\left(\frac{\partial U}{\partial V}\right)_S = P$.

5. CORRECT OPTION (A)

$C_2H_4(g) + 3O_2(g) \rightarrow 2CO_2(g) + 2H_2O(l)$
Here, $\Delta n_g = \Sigma n_g$ (product) $- \Sigma n_g$(reactant) $= 2(-1+3) = -2$

$$\Delta H = \Delta U + \Delta n_g RT$$

OR, $\Delta H - \Delta U = \Delta n_g RT = -2 * 8.314 * 300 = -5000J = -5kJ$

6. CORRECT OPTION (A)

Since, we know that for the entropy of mixing is

$$\begin{aligned}\Delta S_{mix} &= -n_{total}R\boldsymbol{\Sigma}x_i \ln x_i \\ &= -n_{total}R[x_1 lnx_1 + x_2 lnx_2 + x_3 lnx_3] \\ &= -(1+1+2)R\{\frac{1}{4}\ln\left(\frac{1}{4}\right) + \frac{1}{4}\ln\left(\frac{1}{4}\right) + \frac{2}{4}\ln\left(\frac{2}{4}\right)) \\ &= -4R(\frac{1}{2}ln\left(\frac{1}{4}\right) + \frac{1}{2}\ln\left(\frac{1}{2}\right) = 6Rln2\end{aligned}$$

7. CORRECT OPTION(D)

Liquid ⇌ vapour

$$\frac{dP}{dT} = \frac{\Delta H_{vap}}{T_{vap}(V_{vap} - V_{liq})}$$

$or, \frac{dP}{dT} = \frac{\Delta H_{vap}}{T_{vap}(V_{vap})}$ (as $V_{vap} >> V_{liq}$)

$$\Delta H_{vap} = \frac{dP}{dT} T_{vap} V_{vap} = 8 * 10^{-3}(bar\ K^{-1}) * 200(Lmol^{-1}) = 640\ bar\ Lmol^{-1}$$

$= 640 * 100\ Jmol^{-1} = 64kJ\ mol^{-1}$ (since 1 barL=100J)

8. Correct answer is (d).

$H_2O(g)$ + C (graphite) $\leftrightharpoons$ $CO(g) + H_2O(g)$

As the number of mole of gaseous product is more than reactant ($\Delta n_g = 1$)

So there is overall increase in entropy

:: ΔS^o = +ve

:: $T\Delta S^0$ will increase with increase in temperature (A →$T\Delta S°$)

Enthalpy of reaction (ΔH^0) is independent of temperature

ΔH^0 = constant (-B → ΔH^0)

$\Delta G = \Delta H^0 - T\Delta S° = \text{const} - T\Delta S^0$

So with increases of temperature ΔG^0 decreases because ΔS^0 = +ve (C→ ΔG)

9. CORECT OPTION (C)

The vapour of a pure substance, when cooled under a pressure less than its triple-piont pressure solidifies directly.

10. CORRECT OPTION (B)

N V T	N V T	N V T
N V T	N V T	N V T

Canonical ensemble of replies in thermal contact.

11. CORRECT OPTION (B)

Q denotes the heat added to the system and "w" is work done by system.
Then , Q<0, W>0.

12. CORRECT OPTION (B)

Applying Euler theorem Maxwell equation, we get Maxwell relation.

$$dG = VdP - SdT; \left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T$$

$$dA = -SdT - PdV; \left(\frac{\partial S}{\partial V}\right)_T = -\left(\frac{\partial P}{\partial T}\right)_V$$

$$dH = TdS + VdP; \left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$$

$$dU = TdS - PdV; \left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$$

13. **CORRECT OPTION (B)**

Given : for water , ΔH_{vap}= 41kJ/mol

Molar entropy of vaporization ,$\Delta S = \frac{\Delta H_{VAP}}{T_b}$

For water T_b= 373 K(at 1atm)

$$\Delta S = \frac{(41 * 10^3\ Jmol^{-1})}{373K} = 109.9JK^{-1}mol^{-1}$$

14. CORRECT OPTION (A)

Given : Q_h= 90J ; T_h =300K

Since we that

$$\eta = 1 - \left(\frac{Q_C}{Q_H}\right) = 1 - \left(\frac{T_c}{T_H}\right) => \frac{Q_C}{Q_H} = \frac{T_C}{T_H}$$

From option (a), we get,

$$\frac{60}{90} = \frac{200}{300} => \frac{2}{3} = \frac{2}{3}$$

15. CORRECT OPTION (A)

16. CORECT OPTION(C)

$P = \frac{ZRT}{\bar{V}}$ ...(1)

⇨ $\left(\frac{dP}{dT}\right)_V = \left[\frac{d}{dT}\left(\frac{ZRT}{\bar{V}}\right)\right]_V = \frac{R}{V}\left[\frac{d}{dT}TZ\right]$

⇨ $\left(\frac{dU}{dV}\right)_T = T\left(\frac{dP}{dT}\right)_v = [\frac{R}{V}\left[T\left(\frac{dZ}{dT}\right)_V + Z\right]]$ ...(2)

⇨ $\frac{RT^2}{V}\left(\frac{dZ}{dT}\right)_V + \frac{ZRT}{V} - P = \frac{RT^2}{V}\left(\frac{dZ}{dT}\right)_V + P - P = \left(\frac{dU}{dV}\right)_T$

⇨ $\left(\frac{dU}{dV}\right)_T = \frac{RT^2}{V}\left(\frac{dZ}{dT}\right)_V$

17. CORRECT OPTION (C)

At the triple point pressure the liquid phase of a pure substance exists.

18. CORRECT OPTION (C)

According to the transition theory, for activated complex ,one of its vibrational degree of freedom is being converted into translational degree of freedom.
Therefore, required vibration degree of freedom =(3N-6)-1=3N-7.

19. CORRECT OPTION (B)

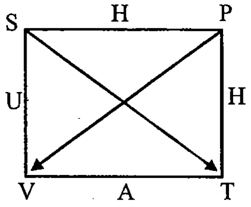
Degree of freedom F=C-P+2
Component C=N-E
Only one phase exist i.e., gaseous phase.
C=N-E=4-2=2
Therefore, F=2-1+2=3

20. CORRECT OPTION (D)

$\oint q = 0$ is not true.
cyclic integral of state function (exact differential) is zero but q is path function (inexact differential). So, cyclic integral of q is not 0.
$\oint w = 0$ is not true, as in the above case above.
heat cannot be converted completely intowork in cyclic process because it is the violation of carnot cycle or carnot engine. Work can be completely converted into heat.(second law of thermodyanamics.)

21. CORRCET OPTION (A)

Maxwell square:



dU =TdS-PdV

Differentiate wrt dV at const. S

$$\left(\frac{\partial U}{\partial V}\right)_S = T\left(\frac{\partial S}{\partial V}\right)_S - P\left(\frac{\partial V}{\partial V}\right)_S$$

$\left(\frac{\partial S}{\partial V}\right)_S = 0$, Because entropy = constant

⇨ $\left(\frac{dU}{dV}\right)_S = 0 - P$

⇨ $\left(\frac{dU}{dV}\right)_S = -P.$

22. CORRECT OPTION (B)

$C_P+C_V = nR$
$300-C_v=10*8.314$
$C_v= 300-83.14=216.86 =217JK^{-1}$

23. CORRECT OPTION (C)

dG= VdP-SdT ....(1)
In an isobaric –isothermal process
dP=0 and dT=0
dG=0 or G=constant
thus, Gibb's function is that physical quantity which remains constant in reversible isobaric process .
From equation (1)
G=G(P,T)

$dG = \left(\frac{\partial G}{\partial P}\right)_T dP + \left(\frac{\partial G}{\partial T}\right)_P dT$ ...(2)

From equation (1) and (2),

$$\frac{\partial}{\partial T}\left(\frac{\partial G}{\partial P}\right)_T = \frac{\partial}{\partial P}\left(\frac{\partial G}{\partial T}\right)_P \quad ; \quad \left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T$$

24. CORRECT OPTION (d)

The chemical potentials are thus the rate of change of free energy per mole at const. temperature and const. pressure.

$dG = \mathrm{VdP} - \mathrm{SdT} + \Sigma\, \mu_i \mathrm{dn_i}$ and constant temperature dT=0 and constant pressure dP=0

$dG = \Sigma\, \mu_i \mathrm{dn_i}$ and $\mu_i = \left(\frac{dG}{dn_i}\right)_{T,P}$

25. CORECT OPTION (A)

Work done in reversible expansion process for an ideal gas
W=-PdV
$P = \frac{nRT}{V}$
If the gas expands from volume V1 to V2 , if the process is isothermal then we amy integrate it from V1 to V2

⇨ $W = -nRT \int_{V_1}^{V_2} \frac{dV}{V}$
⇨ $W = -nRT[lnV]_{V1}^{V2}$
⇨ $W = -nRT \ln\left(\frac{V_2}{V_1}\right) = -2.303\, nRT \log\left(\frac{V_2}{V_1}\right)$

26. Correct option (b)

27. CORRECT OPTION (d)

$W=P\Delta V=P(V_2-V_1)$
A-B WORK:
A→I+I→B
A→I
Work, P=5atm ; V=1 to 1
W=5(1-1)=5(0)=0
I→B
P=1 ; $\Delta V=V_2-V_1$= 5-1=4
$W=P\Delta V$=1(4)=4

28. CORRECT OPTION (A)

$S=k_B\ln W$ (arrangement)

⇨ S/k_B= ln W

⇨ $W=e^{S/k}$

29. CORRECT OPTION (B)

Molar internal energy of combustion=

$$z*\theta*\left(\frac{M}{m}\right)=\frac{50*4*2.5}{0.5}=\frac{50*10*10}{0.5}=\frac{5000}{5}kJ=1000kJ$$

Energy of combustion always has **negative** sign.
Energy of combustion=-1000Kj

30. Correct answer is (c)

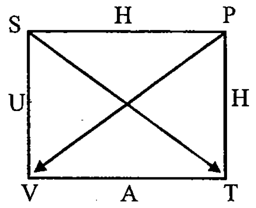
$NO+O_2 \leftrightharpoons NO_2$
[add Ar (g)]

(1) Phase only (gas phase) all are gases
P=1

(2) Component
C = N-E
C=4 -1=3

(3) F=C-P+2
F=3-1+2=4

31. CORRECT OPTION (D)



dH =TdS+VdP

$\left(\frac{\partial H}{\partial S}\right)_P = T$.

32. CORECT OPTION (D)

As we know ,according to euler theorem
For equation,df = Mdx+Ndy .....(1)
F is exact differential only when

$$\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y$$

Given exact differential $df = \frac{1}{y}dx - \frac{x}{y^2}dy$ ...(2)

From eq. (1) and (2), w eget

M=1/y and N=-x/y^2 (follows euler's theorem)

$\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial}{\partial y}\left(\frac{1}{y}\right)\right)_x = -\frac{1}{y^2}$ .....(3)

$\left(\frac{\partial N}{\partial x}\right)_y = -\left(\frac{\partial}{\partial x}\left(\frac{x}{y^2}\right)\right)_y = -\frac{1}{y^2}$ .....(4)

From eq.(3) and (4)

$\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y$

33. CORRECT OPTION (A)

For a multi component open system

$$G = \sum_i n_i \mu_i$$

Differentiating the above eq.

$dG = \sum \mu_i dn_i + \sum n_i d\,\mu_i$ ....(1)

By the fundamental equation ,

$dG = -SdT + VdP + \sum \mu_i dn_i$ .....(2)

Substracting equation (1) and (2)

$-SdT + VdP = \sum \mu_i dn_i$ (Gibbs-Duhem equation)

If T and P are constant,

$\sum n_i d\,\mu_i = 0$ (n$_i$=x$_i$)

$\sum x_i d\,\mu_i = 0$

- ⇨ $x_1 d\mu_1 + x_2\mu_2 = 0$ ….(A)
- ⇨ $dV = \Sigma dn_i V_i + \Sigma n_i dV_i$ ……(3)

Taking V=f(T,P,n$_i$), we have

$dV = \left(\frac{dV}{dt}\right)_{P,n_j} dT + \left(\frac{dV}{dP}\right)_{T,n_j} + \Sigma\left(\frac{dV}{dn_i}\right)_{T,P,n_j,S} dn_i$ (J≠1)

at constant T and P, we have

$$dV = \Sigma\left(\frac{dV}{dn_i}\right)_{T,P,n_j,S} dn_i = \Sigma\, v_1 dn_i$$

Subtracting eq. (3) and (4)

$\Sigma n_i dV_i = 0$ …(4)

For a binary solution, we have

$n_1 dv_1 + n_2 dv_2 = 0$

- ⇨ $\Sigma n_i dv_i = 0$ (n$_i$=x$_i$)
- ⇨ $\Sigma x_i dv_i = 0$
- ⇨ $x_1 dv_1 + x_2 dv_2 = 0$ ……(B)

For a binary mixture relation (A) and (B) are correct.

34. CORECT OPTION (B)

$\Delta G = nRT\ln\frac{P_2}{P_1} => G_2 - G1 = nRT\ln\left(\frac{P_2}{P_1}\right)$

And ,$\Delta\mu = RT\ln\frac{P_2}{P_1}$

- ⇨ $\mu_2 - \mu_1 = nRT\ ln(P_2/P_1)$
- ⇨ $\mu_2 = \mu_1 + nRTln\left(\frac{P_2}{P_1}\right)$

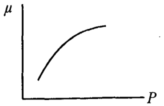
If initial state is standard state then,

$\mu_{T,P} = \mu_T^0 + RT\ln\frac{P}{P_0}$ ……..(1)

$G(T,P) = G_T^0 + nRT\ln\frac{P}{P_0}$ ………(2)

Equation (1) shws that the chemical potential varies with natural logarithm.

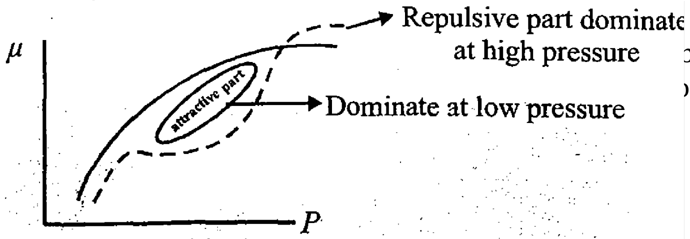
M vs P may be represented as



μ vs P for ideal gas

However , measurement on the real gas shows that the relation between μ andP is not showing exact at very low gas pressure al gas appear ideal behavior at moderate pressure region. The pressure is lower than expected because real gas molecule atarct each other and the measured pressure is power than ideal.

At very high pressure become so densely packed that they begin to rep of chemical potential vs the real pressure may be



μ vs P for ideal gas

35. CORRECT OPTION (d)

For a monoatomic species only translational degree of motion is occur. No vibrational degree of freedom . so, heat capacity is independent of temperature.

36. **CORRECT OTPION (*)**

37. `**CORRECT OPTION(B)**

For a multi component open system

$G = \sum_i n_i \mu_i$

Differentiating the above eq.

$dG = \sum \mu_i dn_i \; + \sum n_i d\, \mu_i$ ....(1)

By the fundamental equation ,

$dG = -SdT + VdP + \sum \mu_i dn_i$ .....(2)

Subtracting the two equations,we get,

$\Sigma n_i d\mu_i = -SdT + VdP$

Where, μ_i= chemical potential ; n_i= number of moles ; I= components

38. CORRECT OPTION (C)

$\Delta G = \Delta H + T\left(\frac{\partial(\Delta G)}{\partial T}\right)_P$ .....(1)

$\Delta G = -nFE$

Therefore, we get,

$\left(\frac{\partial(\Delta G)}{\partial T}\right)_P = -nF\left(\frac{\partial E}{\partial T}\right)_P$ ......(2)

From eq.(1) and(2) we get

$-nFE = \Delta H - nFT\left(\frac{\partial E}{\partial T}\right)_P$ ......(3)

But, $\Delta G = \Delta H - T\Delta S$ .....(4)

$\Delta S = \frac{\Delta H - \Delta G}{T}$

FROM EQ. (3) and (4),we get,

$-T\Delta S = -nFT\left(\frac{\partial E}{\partial T}\right)_P$

- ⇨ $\Delta S = nF\left(\frac{\partial E}{\partial T}\right)_P$
- ⇨ $\left(\frac{\partial E}{\partial T}\right)_P = \frac{\Delta S}{nF}$

So, temperature dependance=$\frac{\Delta S}{nF}$

39. CORRECT OPTION(A)

$\Delta H = \Delta U + \Delta n_g RT$

$\Delta U - \Delta H = -n_g RT$

Fe_2O_3 (s) + 3C (s) → 2Fe (s) + 3CO (g)

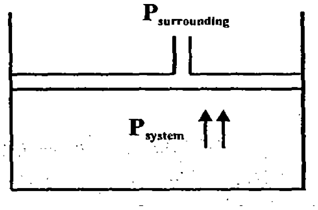
Δn_g= 3-0=3 (only gaseous atom)

ΔU-ΔH=-3RT

40. CORRECT OPTION (B)

$P_{system} > P_{suroundings}$

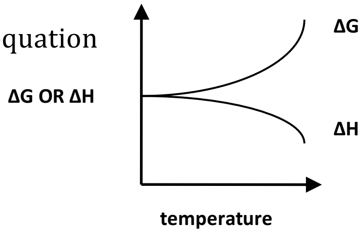
Process of expansion takes place. Work is done by the system on the surroundings.



41. CORRECT OPTION(D)

According to the Gibbs Helmholtz equation

$\Delta G = \Delta H + T\left(\frac{\partial(\Delta G)}{\partial T}\right)_P$



42. CORRECT OPTION (C)

$\Delta G = nRT \ln\frac{P_2}{P_1}$

- ⇨ $\Delta G = nRT \ln\frac{V_1}{V_2}$
- ⇨ $\Delta G = 1 * R * 300 * \ln\left(\frac{1}{4}\right) = -600Rln2$

43. CORRECT OPTION (A)

At triple point vapour pressure of solid A and liquid A are same. So,

$10 - \frac{1800}{T} = 8 - \frac{1400}{T}$

- ⇨ 2=400/T
- ⇨ T=200K.

44. CORRECT OPTION (D)

Option (a),(b) ,(c) talks about the processes which are spontaneous processes.
Option (a) and (c) can be seen through phase diagram of water and (b) is free expansion which is spontaneous.
Option (d) talks about the equilibrium process.
Water ⇌ ice 0^0C ,1 atm
So, this is a non-spontaneous process.

45. CORRECT OPTION (b)

$$\left(\frac{\partial H}{\partial P}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_P + V$$

It shows $\left(\frac{\partial H}{\partial P}\right)_T$ has a dimension of volume.

46. CORECT OPTION (A)

From Maxwell equation ,
dU=TdS-PdV   ....(1)
divide the equation by $(dV)_T$ at constant T

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - P\left(\frac{\partial V}{\partial V}\right)_T$$

⇨ $\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - P$

⇨ $\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V$

⇨ $\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P$ ....(2)

Ideal gas , PV=RT
P=RT/V IN EQ.(2)

$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial\left(\frac{RT}{V}\right)}{\partial T}\right)_V - P$

⇨ $\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{R}{V}\right) - P = \frac{RT}{V} - P = \frac{RT}{\frac{RT}{P}} - P = P - P = 0$

⇨

47. CORRECT OPTION (C)

ΔH_{melt}= 3kJ mol^{-1}=3000J mol^{-1}
T=300K
A(s)→ A(l)
Using Claypeyron equation ,$\frac{dP}{dT} = \frac{\Delta H}{T\Delta V}$

$$\tan\left(\frac{\pi}{3}\right) = \frac{\Delta H}{T\Delta V} => \Delta V = \frac{\Delta H}{T\tan\left(\left(\frac{\pi}{3}\right)\right)} = \frac{3000}{300}\cot\left(\frac{\pi}{3}\right)$$

$$\Delta V = 10\cot\frac{\pi}{3}$$

48. CORECT OPTION (B)

BC is an adiabetic expansion.

49. CORRECT OPTION (D)

U=f(T,V)

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

- ⇨ $\left(\frac{\partial U}{\partial T}\right)_P = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{dV}{dT}\right)_P$
- ⇨ $\left(\frac{\partial U}{\partial T}\right)_P = C_V + \pi \left(\frac{dV}{dT}\right)_P$
- ⇨ NOW, $\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$ => $\left(\frac{dV}{dT}\right)_P = \alpha V$
- ⇨ $\left(\frac{\partial U}{\partial T}\right)_P = C_V + \pi\alpha V$

50. dU=+TdS-PdV

We know that, dS≥ $\frac{\mathrm{dq}}{T}$

dS≥ $\frac{\mathrm{dU+PdV}}{T}$

dU +PdV - TdS ≤ 0

If S & V are constant, then equation (1) becomes $(dU)_{s,v} \leq 0$.

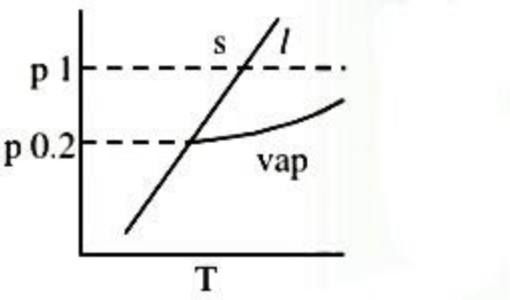
Criteria of spontaniety.

Correct option is (a)

51. Correct option is (d)

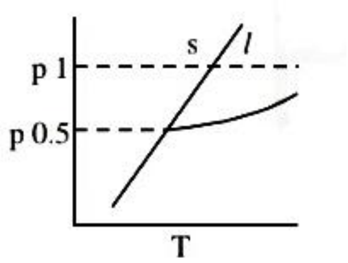
Standard condition means 1 bar pressure

For A



So at 1 bar transition will be solid ⇋ liquid. So number sublimation

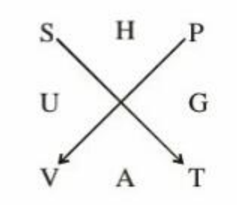
For B



Same explanation as above

52. Correct option is (b)

dH=TdS+ UdP



$$\left(\frac{\partial H}{\partial P}\right)_T = T\left(\frac{\partial S}{\partial P}\right)_T + V$$
$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P .So, \left(\frac{\partial H}{\partial P}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_P + U$$

This is T.E.S. II
Now for given gas
P(V-b)=RT ⇒ PV-Pb=RT
Constant P on differentiating with respect to T
$$P\left(\frac{\partial V}{\partial T}\right)_P - 0 = R \Rightarrow \left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P} \Rightarrow, \left(\frac{\partial H}{\partial P}\right)_T = -T\frac{R}{P} + V$$
now from equation
P(V-b)=RT ⇒ V-b = $\frac{RT}{P}$ ⇒ $\frac{-TR}{P} + V = \frac{TR}{\frac{V-b}{RT}} + V = -V + b + V = b$

So, $\left(\frac{\partial H}{\partial P}\right)_T = b$

53. Correct option is (a)

According to Clapyeron equation

$$\frac{dP}{dT} = \frac{\Delta H}{T\Delta V}$$
if ΔV=0 (because change in volume is zero)
$$\frac{dP}{dT} = \frac{\Delta H}{T(0)} \;;\; \frac{dP}{dT} = \infty$$
; $\frac{dP}{dT}$ represents the slope of phase diagram.

When tan $\theta = \infty$
$\theta = 90^0$

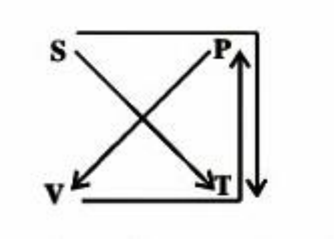
54. Correct option is (a)

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$$

Now, according to reciprocal theorem of partial derivatives

$$\left(\frac{\partial V}{\partial T}\right)_P = \left(\frac{\partial S}{\frac{\partial T}{\partial V}}\right)_P$$

Putting these values in equation (1), we get



$Or, \left(\frac{\partial S}{\partial P}\right)_T = \frac{1}{\left(\frac{\partial P}{\partial S}\right)_T} \Rightarrow \left(\frac{\partial P}{\partial S}\right)_T = -\left(\frac{\partial T}{\partial V}\right)_P$

$Or, \left(\frac{\partial P}{\partial S}\right)_T = -\left(\frac{\partial T}{\partial V}\right)_P$

55. CORRECT OPTION (D)

In one component system 4 phases carnot simultaneously exist at single point.

56. CORRECT OPTION (D)

(i) Phase transition cannot be isoentropic
Solid ⇌ liquid
So, entropy is ging to chage during phase transition

(ii) Phase transition cannot be isochoric as
Solid⇌gas or liquid ⇌ gas
Volume is going to change

(iii) Volume is going to change
As phase transition takes place at constant temperature and pressure.

57. CORRECT OPTION (C)

For any cyclsc process cyclic integral of state is zero.
So, $\oint dU = 0 \; as \; U \; is \; a \; state \; function$

58. CORRECT OPTION (B)

Fugacity of gas is less than P when attractive forces are dominant.It happens at lowP and when T<T_b.

59. CORRECT OPTION (B)

The given engine is working as refrigerator as it is transferring heat from sink (lower temp) to source (higher temp).so, efficiency of refrigerator / coefficient of performance.

$$\eta' = \frac{T_1}{T_2 - T_1} = \frac{100}{300 - 100} = \frac{1}{2}$$

⇨ $\eta' = \frac{|q_c|}{W} => \frac{1}{2} = \frac{5}{W} => W = 10J$

60. CORRECT OPTION(B)

$G = \Sigma\mu_i n_i$

⇨ $G = H - TS$

⇨ H=G+TS

⇨ H= $\Sigma\mu_i n_i + TS$

61. CORECT OPTION (A)

$dG = VdP - SdT + fdL$ ....(1)

Differentiating equation wrt T at constant P,L

$$\left(\frac{\partial G}{\partial T}\right)_{P,L} = -S$$

Similarly differentiating equation (1) wrt L at constant P and T

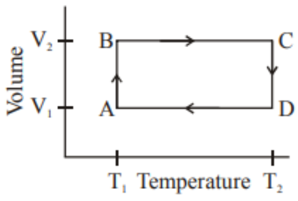
$\left(\frac{\partial G}{\partial l}\right)_{T,P} = F$

Since ,G is a stable function

⇨ $\left[\frac{\partial}{\partial L}\left(\frac{\partial G}{\partial T}\right)_{P,L}\right]_{T,P} = \left[\frac{\partial}{\partial T}\left(\frac{\partial G}{\partial L}\right)_{T,P}\right]_{P,L}$

⇨ $-\left(\frac{\partial S}{\partial L}\right)_{T,P} = \left(\frac{\partial F}{\partial T}\right)_{P,L}$

62. CORRECT OPTION (d)



$W_{TOTAL} = W_{AB} + W_{BC} + W_{CD} + W_{DA}$

Process AB is isothermal

So, $W_{AB} = -nRT_1 \ln \frac{V_2}{V_1}$

Process BC is isochoric

So, $W_{BC}=0$

Process CD is isothermal

So, $W_{CD} = -nRT_2 \ln\left(\frac{V_1}{V_2}\right) = nRT_2 \ln \frac{V_2}{V_1}$

Process DA is isochoric

So, $W_{DA}= 0$.

$$W_{TOTAL} = -nRT_1 \ln\left(\frac{V_2}{V_1}\right) nRT \ln \frac{V_2}{V_1} = nR(T_2 - T_1) \ln\left(\frac{V_2}{V_1}\right)$$

63. CORRECT OPTION (c)

For a reversible process (adiabetic) ,$\Delta S=0$

64. CORRECT OPTION (b)

$$\frac{dP}{dT} = \frac{\Delta H}{T\Delta V}$$

For $H_2O(s) \rightarrow H_2O$ (l)
$\Delta V=V_L-V_S <0$
So, $\frac{dP}{dT} < 0$.

65. CORRECT OPTION (b)

$A=2*10^{-4}K^{-1}$; $\beta=5*10^{-5}$ bar^{-1}
$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P$
$\frac{\alpha}{\beta} = \left(\frac{\partial P}{\partial T}\right)_V = \frac{2*10^{-4}}{5*10^{-5}} = 4$
⇨ $\left(\frac{\partial U}{\partial V}\right)_T = 320 * 4 - 1 = 1279\ bar = 1.279 kbar.$

66. CORRECT OPTION (A)

Fro a closed system the correct statement is
dU=TdS-PdV (Maxwell eqation)

67. Correct option (a)

Condition of first order phase transition is
$\Delta S \neq 0$ AND $\Delta V \neq 0$

68. CORRECT OPTION (A)

Since, the given phases are in compressible. Therefore, the effect of pressure is zero on this phase transistor.

69. CORRECT OPTION (C)

$$dS = \int nC_V dT + \frac{nR}{V}\int l dV$$

$$\Rightarrow \quad \Delta S = nC_{v,m} \ln\left(\frac{T2}{T1}\right) + nRln\left(\frac{V_2}{V_1}\right)$$

So, entropy is proportional to ln V.

70. Correct option (a)

$$\mathrm{dS} = \frac{dq}{T} = \frac{dU + PdV}{T} = \frac{nC_V dT + nRdT - VdP}{T} = \frac{nC_P dT}{T} - \frac{nR}{P} dP$$

$$\Delta S = nC_P ln\frac{T_2}{T} - nRln\frac{P_2}{P_1} \text{ (n= 1, Cp} = \frac{5}{3} R)$$

$T_2 = 600$ K, $P_2 = 4$ atm

$T_1 = 300$ K, $P_1 = 2$atm

$$\Delta S = \frac{5}{2}Rln2 - Rln2$$

$$\Delta S = \frac{3}{2}Rln2$$

71. Correct option (b)

$$\mathrm{P} = \frac{RT}{V_m}\left[1 + \frac{B(T)}{Vm}\right] = RT\left(\frac{\partial lnq}{\partial Vm}\right)_T$$

$$= \frac{1}{Vm}\left(1 + \frac{B(T)}{Vm}\right) = \left(\frac{\partial lnq}{\partial Vm}\right)_T$$

Variable separation and integration ,

$$\int\left(\frac{1}{Vm} + \frac{B(T)}{V^2 m}\right)\partial V_m = \int \partial lnq$$

$$lnVm - \frac{B(T)}{Vm} = lnq$$

On differentiate with respect to temperature at constant volume

$$0-\left(\frac{\partial B}{\partial T}\right)\frac{1}{Vm}=\left(\frac{\partial lnq}{\partial T}\right)_V=U$$

$similarly\ , if\ P=\frac{RT}{Vm}=RT\left(\frac{\partial lnq}{\partial T}\right)_V \Rightarrow\ \int\frac{1}{V}\partial Vm=\int\partial lnq\ \ \Rightarrow ln\,Vm=lnq$

On differentiate with respect to temp at constant volume & multiple by RT^2

$$\Rightarrow 0=\ RT^2\left(\frac{\partial lnq}{\partial T}\right)_V=U_{ideal}$$

$$\mathrm{U}-U_{ideal}=\frac{RT^2}{Vm}\left(\frac{\partial B}{\partial T}\right)_V-0=\frac{RT^2}{Vm}\left(\frac{\partial B}{\partial T}\right)_V$$

72. Correct option (a)

$\mathrm{G^E}=G_{mix}^R-\ G_{mix}^L$

$G_{mix}^R=\mathrm{G^E}+\ G_{mix}^L$

$G_{mix}^L=\mathrm{nRT}\sum x_i ln x_i$

$=4\times 8.314\times 300\left\{\frac{1}{2}ln\frac{1}{2}+\frac{1}{2}ln\frac{1}{2}\right\}$

$=-9976.8ln2=\ -6913.9J=\ -6.913kJ$

$\mathrm{G^E}=-1.5kJmol^{-1}$

Or , $\mathrm{G^E}=-1.5\times 4=-6kJ$

Hence , $\Delta G_{mix}^R=\ \ \mathrm{G^E}+\ G_{mix}^L=-6-6.913=12.913kJ$

73. Correct option is (b)

For adiabatic process, $\Delta U = w = \frac{nR}{1-\gamma}(T_f-T_i)$

$T_1V_1^{\gamma-1}=\ T_2V_2^{\gamma-1}$

$$T_2=\ T_1\left(\frac{V_1}{V_2}\right)^{\gamma-1}=500\left(\frac{5}{50}\right)^{0.4}=199.05K$$

Now, $\Delta U = \frac{nR}{1-\gamma}(T_f - T_i)$

$-\frac{2\times 8.314}{-0.4}(199.05 - 500) = -12510.3\text{J} = -12.5kJ$

74. Correct option is (a)

$\mu_i = \mu_i^0 + RT\ \ln a_i$

Activity, a = $(a_+)^x\ (a_-)^y)$

For $Na_2SO_4 \rightarrow 2Na + SO_4^{-2}$

m 0 0

0 2m m

a= $(\gamma_+ m_+)^x\ (\gamma_- m_-)^y = (\gamma_+^x \gamma_-^y)(\ m_+^x m_-^y)$

a= $(\gamma_\pm)^{x+y}\ ((2m)^x (m)^y) \Rightarrow a = (\gamma_\pm)^{2+1}\ ((2m)^2 (m)^1)$

a= $(\gamma_\pm)^3((4m)^2(m)^{\cdot}) = (\gamma_\pm)^3\ [4m^3] \Rightarrow a = (\gamma_\pm)^3(4m)^3$ (Since , m= 2)

a= $(\gamma_\pm)^3(4\times 2^3) \Rightarrow a = (\gamma_\pm)(2^2\times 2^2) \Rightarrow a = (\gamma_\pm)^3(2^5)$

$\mu_i = \mu_i^0 + RT\ \ln(\gamma_\pm)^3 + RT\ln 2^5$

$\mu_i = \mu_i^0 + 3RT\ \ln(\gamma_\pm)^3 + 5RT\ln 2^5$

75. Correct option is (d)

$\Delta S = nC_p \ln(\frac{T_2}{T_1})$

$\Delta S_1 = nC_p \ln 2$

$\Delta S_2 = nC_p \ln 1.5$

$\Delta S_1 > \Delta S_2$

Entropy is a state function,

$\Delta S = \Delta S_1 + \Delta S_2$

76.Correct option is (c)

$$\frac{n_P}{n_Q} = \frac{3}{1}$$

From Gibb's Duhem equation,

$n_P d\mu_P + n_Q d\mu_Q = 0$

$$\frac{d\mu_P}{d\mu_Q} = \frac{n_Q}{n_P} = -\frac{1}{3};\ d\mu_Q = -3\times10 = -30J/mole$$

77. Correct option is (b)

W_{AB} = -2(46.48 - 23.24) = -46.48 l-atom

At point B, P_BV_B = 2 x 48.48 = 92.96

At point C, P_CV_C = 1x92.96=92.96

Since, in the process BC 'PV' is constant so it is an isothermal process.

$W_{BC} = -nRT\ln\frac{V_2}{V_1} = -PV\ln\frac{V_2}{V_1} = -92.96\ \ln\frac{92.96}{4.648} = -65.07$ l-atm

W_{CD} = -1(23.24-92.96)=69.72 l-atm

W_{DA}=0 (ΔV=0)

Total work = $W_{AB} + W_{BC} + W_{CD} + W_{DA}$ = -46.48-65.07+69.72+0 = 41.83 l-atm

Therefore, total work 4183 J

78 Correct option is (b)

$(C_P - C_v)_{ideal} = nR = P\left(\frac{\partial V}{\partial T}\right)_P$; $(C_P - C_v)_{real} = T\left(\frac{\partial P}{\partial T}\right)_V\left(\frac{\partial V}{\partial T}\right)_P$

$(C_P - C_v)_{real} - (C_P - C_v)_{ideal} = T\left(\frac{\partial P}{\partial T}\right)_V\left(\frac{\partial V}{\partial T}\right)_P - P\left(\frac{\partial V}{\partial T}\right)_P$

$\left(\frac{\partial V}{\partial T}\right)_P\{T\left(\frac{\partial P}{\partial T}\right)_V - P\} = \left(\frac{\partial V}{\partial T}\right)_P\left(\frac{\partial U}{\partial V}\right)_T$

79. Correct option is (d)

In adiabatic process	In isothermal process
PV^{γ} =Constant	PV=Constant

$P \propto \frac{1}{V^{\gamma}}$ $P \propto \frac{1}{V}$

For monoatomic gas $p \propto \frac{1}{V^{\frac{5}{3}}}$

80. Correct option (c)

Vander waal equation

$\left(P+\frac{an^2}{V^2}\right)(V-nb)$= nRT or $\left(P+\frac{a}{Vm^2}\right)(V_m-nb)$= nRT ($V_m$ is the molar volume)

From first thermodynamic equation of state

$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial V}\right)_T - P$ ……(i)

Differentiating eqn (i) with respect to T keeping V constant $\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V_m-b}$

Substituting this value in equation (ii)

$\left(\frac{\partial U}{\partial V}\right)_T = T\frac{R}{V_m-b} - P$ or $\left(\frac{\partial U}{\partial V}\right)_T = P+\frac{a}{V_m^2} - P = \frac{a}{V_m^2}$ $\left(T\frac{R}{V_m-b} = P+\frac{a}{V_m^2}\right)$

81. Correct option (c)

$S^{\text{Excess}} = \Delta S^{observed} - \Delta S^{ideal}$

$\Delta S^{ideal} = -R\left(\frac{1}{2}ln\frac{1}{2}+\frac{1}{2}ln\frac{1}{2}\right)$

$\Delta S^{ideal} = Rln2$; $\Delta S^{observed} = S^{\text{Excess}} + \Delta S^{ideal} = -Rln2 + Rln2 = 0$

82. Correct option (c)

$\mu_1 = \mu^0$ +RT $\ln P_1$ and $\mu_2 = \mu^0$ +RT $\ln P_2$

$$\mu_2 - \mu_1 = RTln\left(\frac{P_2}{P_1}\right)$$

$$\Delta\mu = 8.314\times300ln\left(\frac{2}{1}\right) = 1728.8J$$

83. correct option is (c).

According to phase rule, F=C-P+2

We get,

At equilibrium,

F=0 (at triple point)

0=1-P+2

P=3

84. Correct option (b)

If during a phase transition, entropy and volume of the system remains unchanged, then it is 2nd order phase transition.

If $\Delta S = 0 \ and \ \Delta V = 0$ then 2nd order phase transition

If $\Delta T = 0$, then 1st order phase transition.

8

Statistical Thermodynamics

Hints & Solutions

1. **Correct answer: (a)**

Average energy per particle E =

(Where f = single particle, partition function,) here

$$\frac{df}{dT} = \frac{d}{dT}\frac{AT^m}{V}$$

$$\frac{df}{dT} = \frac{A}{v} mT^{m-1} \text{ ....2}$$

Put this value in equation (I), we get , $E = \frac{KT^2}{\frac{AT^m}{v}}\frac{A}{V}mT^{m-1} = mkT$

2. **Correct answer: (d)**

The virial expression for a real gas can be written as

$$\frac{P\bar{V}}{RT} = 1 + B_p P + C_p P^2 \text{ .... 1}$$

$$\frac{P\bar{V}}{RT} = 1 + \frac{B_v}{v} + \frac{C_v}{v} \text{ ....2}$$

(From equation (2))

$$P = \frac{RT}{v}\left(1 + \frac{Bv}{v} + \frac{Cv}{V^2}....\right)$$

Substitute this 'P' in R.H.S. of equation (1)

$$\frac{R\bar{V}}{RT} = 1 + B_p \frac{RT}{v}\left(1 + \frac{Bv}{v} + \frac{Cv}{v^2}....\right) + \left(1 + \frac{Bv}{v} + \frac{Cv}{v}....\right)$$

Or, $\frac{R\bar{V}}{RT} = 1 + B_p \frac{RT}{v} + \frac{1}{v^2}\left(B_p B_v RT + Cp\left(RT\right)^2\right) +$ ....

Compare Ist term on R.H.S of equation (1) and (3)

$Bv = B_p(RT)$; $Bv = aBp$ (hence = RT)

3. **Correct answer: (a)**

standard deviation of Maxwell's speed = $= \sqrt{\left\langle V^2 \right\rangle - \left\langle V^2 \right\rangle} \quad = \sqrt{r_{rms}^2 - v_{avg}^2}$

QUANTA POINT

$$= \sqrt{\frac{3RT}{M} - \frac{8RT}{\pi M}} = \sqrt{\left(3 - \frac{8}{\pi}\right)\frac{RT}{M}} = \sqrt{\left(3 - \frac{8}{\pi}\right)}\sqrt{\frac{RT}{M}}$$

$$=0.67\sqrt{\frac{RT}{M}} = 0.7\sqrt{\frac{RT}{M}}$$

4. Correct answer is (c)

Population P $\propto\ e^{-\frac{E}{KT}}$

Therefore at constant temperature lower the energy (E) higher will be population.

$E_A > E_B$

$P_A\,(T_1) < P_B\,(T_1)$, $P_A\,(T_2) < P_B\,(T_2)$

Also higher the energy value, higher will be the change in population ratio when temperature is changed from T_2 to T_1

$$\frac{P_A(T_1)}{P_A(T_2)} > \frac{P_B(T_1)}{P_B(T_2)} \Rightarrow \frac{P_A(T_1)}{P_A(T_1)} > \frac{P_B(T_2)}{P_B(T_2)}$$

5. Correct answer is (c)

Since θ, $\propto\ \frac{1}{\mu r^2}\ when\ \mu = \frac{m_1 m_2}{m_1+m_2}$.

When r is same then , θ, $\propto\ \frac{1}{\mu}$

$$\frac{[\theta_r,(H_2).\theta_r(D_2)]}{[\theta_r(HD)]^2} = \frac{\mu_{HD}^2}{\mu_{H_2}\mu_{D_2}} = \frac{\frac{1\times 2}{1+2}}{\left(\frac{1\times 1}{1+1}\right)\left(\frac{2\times 2}{2+2}\right)} = \frac{\left(\frac{2}{3}\right)^2}{\frac{1}{2}\times 1} = \frac{8}{9}$$

6. Correct answer is (d).

In order to have 10 unit total energy only 2 combinations of selecting particles are possible

(i) One particle with 1 unit energy and 3 particles with 3 unit energy each

Therefore, number of ways possible = ${}^4C_1$ x ${}^3C_3$ = 4×1=4 ways

(Because first particle can be selected in 4 ways next 3 particles from remaing 3-particles can be selected in only 1 way)

(ii) 2 paticles with 2 unit energy each and 2 particles with 3 unit energy each

Therefore, number of ways possible = (selection of 2 particles out of 4-particles) × (selecting of 2 particles out of remaining 2-particles) = ${}^4C_2$ x ${}^3C_2$ = 6×1=6 ways

Therefore, total number of ways = 4 + 6 = 10 ways.

7. Correct answer is (c)

k.E = $\frac{1}{2}mV^2$

According to question ,

1MeV= $\frac{1}{2}M_\alpha S_1^2$
2MeV= $\frac{1}{2}M_\alpha S_2^2$
Dividing equation ii by i
$\left(\frac{S_2}{S_1}\right)^2 = 2$, $S_2 = \sqrt{2}\ S_1$

8. Correct answer is (b).
The relative population in two states with energy E_1 and E_2 satisfy Boltzmann distribution law
$\frac{n_1}{n_2} = \frac{g_1}{g_2}\ e^{\frac{[E_1 - E_2]}{K_BT}}$ ....(1) [where, g_1 and g_2 are degeneracy]

Given : $\frac{n_1}{n_2}$ =($\frac{3}{2}$) exp [-(E_1 - E_2)/k_bT] ……. (2)

Compare equation (1) and (2), we get, = $\frac{g_1}{g_2} = \frac{3}{2}$

The value of $\frac{g_2}{g_1} = \frac{2}{3}$

9. Correct answer is (d)
We know that , $\epsilon_{vib} = \frac{1}{1 - e^{\frac{-hv}{k_BT}}}$ …………1
hv= k_BT ………2
From equation 1 and 2

$$\epsilon_{vib} = \frac{1}{1 - e^{\frac{-k_BT}{k_BT}}} = \frac{1}{1 - \frac{1}{e}}$$

10. Correct option (c)
S= $K_B lnW$ …………..1

Where w = arrangement

W= $\frac{6!}{0!1!2!3!} = \frac{6\times5\times4\times3\times2\times1}{1\times2\times3\times2\times1} = 60$

From equation 1 , S= $K_B ln60$

11. Correct option (d)

Rotational partition function
Z_{rot} =2(Z'even Zeven + Z'odd Zodd) …….i
For H_2 molecule,

spin 'i' equal to ½

So, Z'even = $\frac{i}{2i+1}$ and Z odd = $\frac{i+1}{2i+1}$

Zeven = $\sum_{J=\,0,2,4.....}(2J+1)e^{-\beta Bhc1(J+1)}$
and Zodd = = $\sum_{J=\,1,3,5.....}(2J+1)e^{-\beta Bhc1(J+1)}$

$$H_2\ (i=1/2)\begin{cases}\text{ortho } Z'\text{odd} = \frac{\frac{1}{2}+1}{2} = \frac{3}{2}\\ \text{para, } Z'\text{even} = \frac{\frac{1}{2}}{2} = \frac{1}{4}\end{cases}$$

Put the value Z'even Zeven Z'odd Zodd in equation (i)

$$\frac{1}{4}\left[\sum_{J=\,0,2,4.....}(2J+1)e^{-\beta Bhc1(J+1)} + 3\sum_{J=\,1,3,5.....}(2J+1)e^{-\beta Bhc1(J+1)}\right]$$

12. Correct option (b)

W = $\frac{(100)^{100}}{100!}$ (for boson particle)

S= = $K_B lnW$ =$K_B ln\frac{(100)^{100}}{100!} = K_B(ln100^{100} - ln100!)$

kB (100ln 100-100ln100+100)=10^2 kB

13. Correct option (c)

Given: total particles = 6 (N) and states {1, 2, 3}

$n_1 = 1$, $n_2 = 2$, $n_3 = 3$

So, possible arrangements = $\frac{N!}{n_1!n_2!n_3!} = \frac{6!}{1!2!3!} = 60$

14. Correct option (a)

$K_BT = 1$

$$\frac{n_j}{n_i} = \frac{g_j}{g_i}e^{\frac{\Delta\in}{k_bT}} = \frac{2}{1}e^{-2} = 2e^{-2}$$

15. Correct option (c)

Number of energy levels (g_i) = 2

The number of ways of distributing = $2^N = 2^4 = 16$
Number of molecules (N_i)= 4

(since, it is not given either particles are distinguisable or indistinguishable, therefore, we will consider it as distinguishable)

16. Correct option (b)

Since rotational partition function is given by

$q = \frac{k_BT}{\sigma hcB}$ where, $B = \frac{h}{8\pi^2 Ic}$

$q = \frac{k_BT}{\sigma hc\frac{h}{8\pi^2 Ic}} = \frac{8\pi^2 IKT}{\sigma h^2} = q \propto \frac{I}{\sigma}$
Hence, two factor should be considered
(i)$I \propto \mu$

(ii) σ(symmetry number)

In present case, H-C=C-H has smallest μ (reduced mass) also having σ= 2. Therefore, H-C=C-H will have smallest rotational partition function .

17. Correct answer is (b)

A is given by

$$A = \frac{N_AKT}{h}\frac{Q^{\#}}{Q_AQ_{BC}}$$

$$\Rightarrow \frac{N_AKT}{h}.\frac{(q_{rot})^3(q_{trans})^3(q_{vib})^2}{(q_{trans})^3[(q_{trans})^3(q_{rot})^3(q_{vib})^2]}$$

$$\Rightarrow \frac{N_AKT}{h}\frac{(q_{rot})^{\cdot}(q_{vib})}{(q_{trans})^3} = 6\times10^{23}\times10^{13}\frac{(10)(1)}{10^{30}} = 6\times10^7$$

18. Correct option (a)

$S = k_b \ln W$

$S = k_b \ln W$

$S/k_b = \ln W$

$W = e^{\frac{S}{k_B}}$

19. Correct option (d)

For vibrational partition function $q_{vib} = \frac{e^{\frac{-hv}{2kT}}}{1-e^{\frac{-hv}{KT}}}$

For condition ($\theta = hv/k$). so, from equation i, we get

$q_{vib} = \frac{e^{\frac{-hv}{2kT}}}{1-e^{\frac{-hv}{KT}}}$

case 1 : T is very low so that $\frac{\theta}{T} \ggg 1$. Then $e^{-\frac{\theta}{T}}$ is neglected compared with unity in the denominator of equation ii, we get

qvib $= e^{-\frac{\theta}{2T}}$ (at low temperature)

Case 2 . T is very high so that $\frac{\theta}{T} \lll 1$. then the exponential in the denominator can be expand as series retaining only the first two terms .

$e^{-\frac{\theta}{T}} = 1 - \frac{\theta}{T}$

$q_{vib} = \frac{\theta}{T} e^{-\frac{\theta}{2T}}$

20. Correct option (d)

The number of microstate $= \frac{n!}{r!n-r!} = \frac{4!}{2!4-2\,!}$

$= \frac{4\times3\times2\times1}{2\times2} = 6$

There are 4 given staes and no of particles 2 possible distribution .

21. Correct option (c)

Partition function is given by q = $\sum_j g e^{\frac{-\epsilon_g}{kT}}$

Q = $g_0 + g_1 e^{\frac{-\epsilon_1}{kT}} + g_2 e^{\frac{-\epsilon_2}{kT}} + \cdots \ldots\ldots\ldots\ldots g_j e^{\frac{-\epsilon_j}{kT}}$

q=$g_1 + g_2 + g_3 + \cdots \ldots\ldots g_j$

q = $\sum_j g_j$

22. Correct option (d)

neglecting zero point energy , q = $(1- e^{\frac{-hv}{kT}})^{-1} = (1-e^{-1})^{-1}$ (hv= kT)

Probability is given

$$\Rightarrow \frac{N_i}{N} = \frac{1}{q}e^{\frac{-\Delta \in}{kT}} = \frac{1}{(1-\mathrm{e}^{-1})^{-1}}e^{\frac{-hv}{kT}} = (1-\mathrm{e}^{-1})^{-1}e^{-1} = e^{-2}(\mathrm{e}-1)\cdot$$

23. Correct option (c)

Maxima in the curve corresponds to most probable speed of the gas .

$$C_{MR} = \sqrt{\frac{2RT}{M}}$$

As $M_{Ne} < M_{Ar} < M_{Kr}$.

So , $C_{(M.P)Ne} < C_{(M.P)Ar} < C_{(M.P)Kr}$

So , curve C corresponds to Ne , B to Ar and A to Kr

24. Correct option (b)

f= Ave^{BT}. …….1

Since , average energy = $NKT^2\left(\frac{\partial lnf}{dT}\right)_V$

Therefore , average energy per particle = $KT^2\left(\frac{\partial lnf}{dT}\right)_V$………2

From equation 1 , we get , $\left(\frac{\partial lnf}{dT}\right)_V = \left(\frac{\partial lnA}{dT}\right)_V + \left(\frac{\partial lnV}{dT}\right)_V + \left(\frac{\partial lne^{BT}}{dT}\right)_V$ = 0 +0+B

From equation 2 , average energy per particle= $KT^2(B) = BKT^2$

25. Correct option (b)

Since Boltzmann formulation deals with whole system containing N number of particles Therefore, f should be replaced by fN N! {Since on incorporating condition of indistinguishability total number of arrangements changes by 1 N! }

26. Correct option (d)
entropy and heat capacity
since , entropy change in partition function is compensated by change in total energy and in heat capacity differentiation with respect to temperature lead to cancellation of constant shift in energy .

27. Correct option (b)

standard deviation of Maxwell's speed = $\sqrt{\langle V^2\rangle - \langle V\rangle^2}$

$$= \sqrt{r_{rms}^2 - V_{avg}^2}$$

$$= \sqrt{\frac{3RT}{M} - \frac{8RT}{\pi M}} = \sqrt{\left(3 - \frac{8}{\pi}\right)\frac{RT}{M}} = \sqrt{\left(3 - \frac{8}{\pi}\right)}\sqrt{\frac{RT}{M}}$$

$$=0.67\sqrt{\frac{RT}{M}} = 0.7\sqrt{\frac{RT}{M}}\ ,\ \sigma_c \propto \sqrt{T}$$

28. Correct option (b)

$$\frac{n_2}{n_1} = exp\left(\frac{-hv}{KT}\right)$$

$$\frac{n_2}{n_1} = \frac{\frac{1}{2n_1}}{n_1} = \frac{1}{2}(given\ )$$

$$\frac{1}{2} = exp\left(\frac{-hv}{KT}\right) \Rightarrow ln\ \left(\frac{1}{2}\right) = \frac{-hv}{KT}$$

$$T = \frac{-hv}{K_B ln2} \Rightarrow T = \frac{hv}{K_B ln2}$$

29. Correct option (d)

The single – partition translational partition function (f) = $\frac{V}{\lambda^3}$ for an ideal gas in a fixed volume V

f∞λ^{-3} , $given$ f~(λ_{th})^n

n= -3

30. Correct option (d)

↑↑↓↓↓ total spin ½ particle

Weight of configuration = $\frac{5!}{3!2!} = \frac{5\times4\times3!}{3!2!} = 10$

31. Correct option (c)

Since , zero point energy = 0

$$q = \frac{1}{1 - e^{\frac{-\Delta E}{kt}}}\ (given\ \Delta E = K_B T)$$

$$q = \frac{1}{1 - e^{\frac{kt}{kt}}} = \frac{1}{1 - e^{-1}} = \frac{1}{1 - \frac{1}{e}} = \frac{1}{\frac{e-1}{e}}$$

$$q = \frac{e}{e-1}$$

32. Correct option (d)

$(no\ of\ arrangments)^{C}_{classical} > (no\ of\ arrangments)^{A}_{fremions} > (no\ of\ arrangments)^{B}_{bosons}$

$S_C > S_A > S_B$

33. Correct option (d)

$$\frac{N_2}{N} = \frac{g_2 e^{-\beta E_2}}{g_1 e^{-\beta E_1} + g_2 e^{-\beta E_2}} \Rightarrow \frac{g_2 e^{-\beta (E_2 - E_1)}}{g_1 + g_2 e^{-\beta (E_2 - E_1)}} \left\{ \frac{N_2}{N_1} = \frac{g_2}{g_1} \Rightarrow N_2 = NP_2 = \frac{N g_2 e^{-E_2}}{\sum g_i e^{-\beta E_2}} \right\}$$

$$\frac{2e^{\frac{-400}{420}}}{4 + 2e^{\frac{-400}{420}}} = \frac{1}{2e^{\frac{-400}{420}}} = \frac{1}{1+2e}$$

34. Correct option (d)

$^3P_2$

Degeneracy = $(2\times2+1) = 5$

S= $K_B ln q_e$

For electron ground state , $q_e = g_e$

S= $K_B ln q_e = k_B ln5$

35. Correct option (c)

For distinguishable particles ,

W= $N!\, \pi_i \frac{g_i{}^{ni}}{n_i!}$

W= $4! \frac{g_0{}^{n0}}{n_0!} \times \frac{g_1{}^{n1}}{n_1!} = 4! \times \frac{2^3}{3!} \times \frac{3^1}{1!} = 96$

36. Correct option (c)

$$q_t = \frac{V}{\lambda^3}, \lambda = \frac{h}{\sqrt{2\pi m k_b T}}$$

$$\lambda = \frac{6.626\times10^{-34}}{\sqrt{2\times3.14\times4\times1.66\times10^{-27}Kg\times1.38\times10^{-23}JK^{-1}\times298K}}$$

$$= \frac{6.626\times10^{-24}}{\sqrt{2\times3.14\times1.66\times1.28\times10^{-25}JK^{-1}\times298K}}$$

q=$\frac{100\times10^{-6}m^3}{(5.05\times10^{-11})^3m^3} = 0.7764\times10^{-27}$

q=7.8×10^{26}

37. Correct option (b)

[A-A(0)]= $-NK_BTlnq$

Given : N = 10 , q= q = 2s+1 =$2\times1 + 1 = 3$

[A-A(0)]= -$10k_bTln(3)$

38. Correct option (b)

$$\lambda = 1.6\times10^{-11}m, q = \frac{V}{\lambda^3} = \frac{1L}{(1.6\times10^{-11}m)^3} = \frac{10^{-3}m^3}{(1.6)^3\times10^{-33}} = \frac{10^{30}}{(1.6)^3}$$

= $0.244\times10^{30} = 2.44\times10^{29}$

39. Correct option (a)

$$q = \frac{kT}{\sigma Bhc} \Rightarrow q \propto \frac{1}{B}\ and\ B\ \propto \frac{1}{I}$$

q $\propto$ I

I (H_2) is smallest ; q(H_2) is smallest

40. Correct option (b)

For linear molecule , $U_{trans} = \frac{3}{2}RT$

$U_{rot} = RT$ (T >> θ_r)

$U_{vib} = RT$ (T >> θ_v)

$U_{trans} : U_{rot} : U_{vib} = \frac{3}{2}RT : RT : RT = \frac{3}{2} : 1 : 1$

41. Correct option is (a)

Total number of population in excited state is N'= $\frac{1}{q}e^{\frac{-\gamma hB'_0}{2K_BT}}$

Total number of population in ground state is N = $\frac{1}{q}e^{\frac{-\gamma hB^{\cdot}_0}{2K_BT}}$

Partition function q = 1 in both the cases.

The population ratio $\frac{N'}{N} = e^{\frac{-\gamma hB'_0}{2K_BT}} e^{\frac{-\gamma hB^{\cdot}_0}{2K_BT}} = e^{\frac{-\gamma h(B^{\cdot}_0 - B'_0)}{2K_BT}}$

Hence, $\frac{N'}{N} = \frac{e^{\gamma\hbar}}{2k_BT}$ (5.5)

Taking In on both sides, we get

ln $\frac{N'}{N} = \frac{5.5\ \gamma\hbar}{2k_bT}$

[But in answer 1/2 part is absent, which is obtained from γħBM$_I$ value. M$_I$ values for protons are +1/2 and -1/2]

42. Correct option (a)

From Sackur Tetrode Equation the molar entropy for monoatomic gas A is

$S_m^0 A$ = R [-1.1541 $+\frac{5}{2}$lnT+$\frac{3}{2}$ln $M_A - ln\ \frac{P}{P_0}$]

The molar entropy for monoatomic gas B is
$S_m^0 B$ = R [-1.1541 $+\frac{5}{2}$lnT+$\frac{3}{2}$ln $M_B - ln\ \frac{P}{P_0}$]
The difference between two standard molar entropy is
$S_m^0 A - S_m^0 B = \frac{3}{2}R\{\ \ln M_A - \ln M_B\} = \frac{3}{2}Rln2$

43. Correct option is (c)
The fraction of molecules in the excited state is equal to the ratio of molecules in the excited state to the total number of molecules.

$$\frac{n_1}{N} = \frac{n_1}{n_0 + n_1} = \frac{g_1 exp\left(-\frac{\epsilon_1}{k_BT}\right)}{g_0 exp\left(-\frac{\epsilon_0}{k_BT}\right) + g_1 exp\left(-\frac{\epsilon_1}{k_BT}\right)}$$

$$\frac{n_1}{N}=\frac{2exp\left(-\frac{\epsilon_1}{k_BT}\right)}{exp\left(-\frac{\epsilon_0}{k_BT}\right)+exp\left(-\frac{\epsilon_1}{k_BT}\right)}$$

$$\frac{n_1}{N}=\frac{2exp\left(-\frac{(\epsilon_1-\epsilon_0)}{k_BT}\right)}{1+2exp\left(-\frac{(\epsilon_1-\epsilon_0)}{k_BT}\right)} \quad ....(1)$$

Since $\epsilon_1 - \epsilon_0 = \Delta\epsilon \ and \ T \xrightarrow[gives]{} \infty$. Therefore equation 1 gives

$$\frac{n_1}{N}=\frac{2}{1+2}=\frac{2}{3}$$

44. Correct option is (c)

Residual entropy, $S = k_B \ln W^{NA}$ where W = arrangement

Arrangement for solid OCS,

O=C=S

S=C=O

Arrangement, W = 2

$S = k_B \ln(2)^{NA}$; $S = N_A k_B \ln 2$

$S = R\ln 2$; $S = 8314 \times 0.693 \frac{\text{J}}{\text{K}} = 5.7628\,\frac{\text{J}}{\text{K}}$

45. Correct option (b)

Entropy in terms of internal energy $U\text{-}U_{(0)}$ and canonical partition function Q

$$S=\frac{U-U(0)}{T}+k\ln Q$$

Since canonical partition function Q for distinguishable particles is given as q^N

$$S=\frac{U-U(0)}{T}+k\ln q^N$$

For monoatomic gas U-U (0) = 3/2nRT and $q=\frac{V}{\lambda^3}$, where $\lambda=\frac{h}{\sqrt{2\pi mKT}}$ h

Put these value in equation (1)

$$S=\frac{\frac{3}{2}nRT}{T}+Nk\ln\frac{V(2\pi mKT)^{3/2}}{h^3}$$

$$S=\frac{3}{2}\,nR+n\,R\,\ln\left\{V(2\pi mkT)^{\frac{3}{2}}\middle|h^3\right\}$$

46. Correct option (d)

For macro-canonical system, Uniform distribution function is the correct probability distribution function for energy.

9

Atomic and Molecular Term Symbols

Hints & Solutions

1. Correct option (b)

Given electronic configuration : $(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(2\sigma_u)^2(2\pi_u)^1(2\pi_u)^1$

Here $(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(2\sigma_u)^2$ belongs to closed shell only valence shell is considered while writing term symbol.

Here, ^ = $\sum\lambda = +1+(-1) = 0 \qquad \Rightarrow \sum$

S= $\frac{1}{2}+\frac{1}{2}=1$

or, 2s+1=3

Reflection under plane containing nuclei = $(-)\times(+)=(-)$ and $u \times u$ **= g**

term symbol, $3\sum_g^-$

2. Correct option (b)

for ^3D

2S+1=3 $\Rightarrow$ 2S= 3-1

$\Rightarrow$ S = 1

L = 2

J can have values from |L + S| ....|L-S|

|2 + 1| ....|2-1|

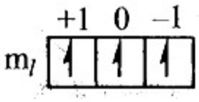
3 2 1

QUANTA POINT

total values are 3.

3. Correct option (d)

$N \rightarrow 1s^2 2s^2 2p^3$



L= 1+0-1 = 0 term defined as S

s=3/2
2s+1= 4
J = (L+S) = 0+3/2 = 3/2

Therefore, ground state term symbol is $^4S_{3/2}$

4. Correct option (b)
for allowed transition

(i) $\Delta \wedge = 0, \pm 1$
(ii) $(+) \leftrightarrow (+)$ or $(-) \leftrightarrow (-)$
(iii) $g \leftrightarrow u$ or $u \leftrightarrow g$

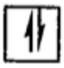
transition (B) and (D) follows all the criteria for allowed transitions.

5. Correct option (c)
for electric transition, selection rule is as follows

(i) $\Delta S = 0$
(ii) $\Delta l = \pm 1$
(iii) $\Delta J = 0, \pm 1$

$^3F \rightarrow {}^3D$ is allowed transition, because, $\Delta S = 0$ and $\Delta l = -1$

6. Correct option (c)
$He \rightarrow 1s^2$

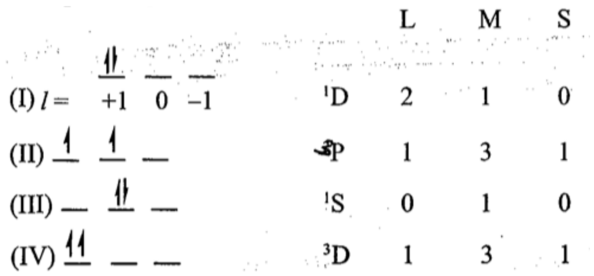


L=0, S=0
J = |L+S| = 0

s= 0
2s+1=1

thus the term symbol, $^1S_0$

7. Correct option (d)
for np^2 configuration, (microstates)



		L	M	S
(I) $l =$ +1 0 −1	^1D	2	1	0
(II)	^3P	1	3	1
(III)	^1S	0	1	0
(IV)	^3D	1	3	1

the configuration (IV) violates Pauli's Principle, hence term symbol ^3D is not possible.

8. Correct option (d)

for electronic configuration, ns^1np^1

$L = 1$

$S = 1$

Hence, $2s+1 = 3$

$J = |L-S| = |1-1| = 0$ (for less than half filled orbital)

Thus, term symbol will be: $^3P_0$

9. Correct option (b)

for electric transition, selection rule is as follows

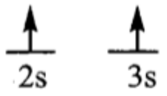
(i) $\Delta S=0$

(ii) $\Delta l = \pm 1$

$^3S \rightarrow {}^3P$ follows all the selection rules.

10. Correct option (a)

Be (in excited state)→ $1s^2\, 2s^1\, 3s^1$



$s= \frac{1}{2} + \frac{1}{2} = 1$

multiplicity = $2s+1 = 3$

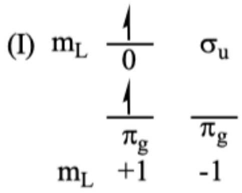
$L = 0+0 = 0$

$J = |L+S| \ldots\ldots\ldots |L-S| = |0+1| \ldots . |0-1| = 1$

Hence, term symbol is $^3S_1$

11. Correct option (a)

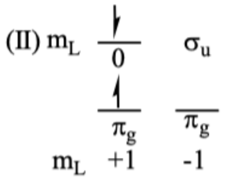
the arrangements for $[1\pi_g]^1[3\sigma_u]^1$ configuration are



$s= 1$, $2s+1 = 3$

$L=1 \rightarrow \Pi$ term

Spectroscopic term → $^3\Pi$



s= 0, 2s+1 = 1
L=1 → Π term
Spectroscopic term → $^1\Pi$

Thus, one possible term symbol is $^1\Pi$

12. Correct option is (a)

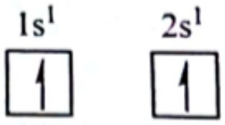
$1s^2, 2s^2, 2p^4$

Number of microstate for $P^4 = \frac{6!}{4!(6-4)!} = 15$

$^1s = 1\times1 = 1 \Rightarrow {}^3p = 3 \times 3 = 9$

Thus, remaining microstate are 5 which comes from $^1D = 1\times5 = 5$

13. Correct option (c)



s= ½ + ½ = 1
multiplicity = 2s+1 = 3

$J = |L+S| \ldots\ldots\ldots |L-S| = |0+1|\ldots.|0-1| = 1$

Hence, term symbol is $^3S_1$

14. Correct option (a)

Selection rule for atomic transition

- (i) $\Delta S=0$
- (ii) $\Delta l = \pm1$
- (iii) $\Delta J = 0, \pm1$

(a) $\underset{\substack{S=1\\L=3\\J=4}}{{}^3F_4} \rightarrow \underset{\substack{S=1\\L=2\\J=3}}{{}^3D_3}$ So, $\Delta S = 0;\ \Delta L = -1;\ \Delta J = -1$ (allowed transition)

(b) $\underset{\substack{S=1\\L=3\\J=4}}{{}^3F_4} \rightarrow \underset{\substack{S=0\\L=2\\J=3}}{{}^1D_3}$ So, $\Delta S = -1;\ \Delta L = -1;\ \Delta J = -1$ (not allowed transition)

(c) $\underset{\substack{S=1\\L=3\\J=4}}{{}^3F_4} \rightarrow \underset{\substack{S=1\\L=1\\J=4}}{{}^3P_4}$ So, $\Delta S = 0;\ \Delta L = -2;\ \Delta J = 0$ (not allowed transition)

(d) $\underset{\substack{S=1\\L=3\\J=4}}{{}^3F_4} \rightarrow \underset{\substack{S=1\\L=2\\J=2}}{{}^3D_2}$ So, $\Delta S = 0;\ \Delta L = -1;\ \Delta J = -2$ (not allowed transition)

15. Correct option (d)

$$N_2^+ \Rightarrow \sigma_{1s}^2\ \sigma_{1s}^{*2}\ \sigma_{2s}^2\ \sigma_{2s}^{*2}\ \pi_{2px}^2 = \pi_{2py}^2\ \underbrace{\sigma_{2pz}^1}_{\text{gerade orbital}}$$

$\Lambda = 0$ i.e. Σ

$S = \dfrac{1}{2}\quad 2S+1 = 2\times\dfrac{1}{2}+1 = 2$

As σ_{2pz} orbital is symmetric, (+) is used.

Thus, term symbol of N_2^+ is ${}^{2S+1}\Lambda_{g/u}^{+/-} = {}^2\Sigma_g^+$

16. Correct option (c)

The atomic term is given by ^{2S+1}L
so comparing this with given term
we get,
$2S+1=4 \Longrightarrow S=3/2$ and $L= 3$ (for F).

Thus, number of microstates $= (2S+1)\times(2L+1)$
$= \left(2\times\frac{3}{2}+1\right)\times(2\times 3+1)$
$= (4)\times(7)$
$= 28$

17. **Correct option (a)**
Since, $\Phi = h\upsilon - e\times E_s$
Where Φ is work-function
υ is frequency
E_s is stopping potential
e is charge of an electron

using above equation for two frequencies and stopping potentials, we get,

$\Rightarrow h\upsilon_1 - e\times E_{s_1} = h\upsilon_2 - e\times E_{s_2}$

on solving we get,

$\upsilon_2 = \frac{e}{h}\left(E_{s_2} - E_{s_1}\right) + \upsilon_1$

thus, $\upsilon_2 = 2.4\times10^{14}\ (0.72) + \ 6.0\times10^{8}\times10^{6}\text{Hz}$

$\upsilon_2 \approx 7\times10^{14} Hz$ or $7\times10^{8} MHz$

10

Kinetic Theory of Gases

Hints & Solutions

1. Correct option (c)

for ideal gas Joule - Thomson coefficient $\mu_{JT} = \left(\frac{\partial T}{\partial P}\right)_H = 0$

so we cannot product cooling or heating under iso- enthalpic process

under the given process . PV^a = constant ..... (1)

For ideal gas, $PV^a = nRT$ ......(2)

substituting P from equation (2) in (1)

we get, TVa-1 = constant

or $T_1V_1^{a-1} = T_2V_2^{a-1}$

therefore, $\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\alpha-1}$

$\Rightarrow$ $\log\left(\frac{T_2}{T_1}\right) = (\alpha-1)\log\left(\frac{v_1}{v_2}\right)$ .....(3) [since $V_2 > V_1$]

now, in equation (3)

$\Rightarrow$ $\log\left(\frac{v_1}{v_2}\right) = -ve$

So for T2 > T1 (heating)
a must be less than 1. Also expansion causes decreases in decrease in pressure of gas, this is possible for a > 0 as PV^a = constant

QUANTA POINT

we get, TV^{a-1}= constant

or $T_1V_1^{a-1} = T_2V_2^{a-1}$

therefore, $\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{a-1}$

$\Rightarrow$ $\log\left(\frac{T_2}{T_1}\right) = (a-1)\log\left(\frac{V_1}{V_2}\right)$ ….. (3) [since $V_2>V_1$]

now, in equation (3)

$\Rightarrow$ $\log\left(\frac{V_1}{V_2}\right) = -\text{ve}$

so, for $T_2>T_1$ (heating)

a must be less than 1. Also expansion causes decreases in decrease in pressure of gas, this is possible for a>0 as PV^a = constant

2. Correct option (a)

Standard deviation in speed = $\sqrt{\langle V^2\rangle - \langle V\rangle^2}$

$$= \sqrt{r_{rms}^2 - V_{avg}^2}$$

$$= \sqrt{\frac{3RT}{M} - \frac{8RT}{\pi M}}$$

$$= \sqrt{\left(3-\frac{8}{\pi}\right)\frac{RT}{M}}$$

$$= \sqrt{\left(3-\frac{8}{\pi}\right)}\sqrt{\frac{RT}{M}}$$

$$= 0.67\sqrt{\frac{RT}{M}} \approx 0.7\sqrt{\frac{RT}{M}}$$

3. Correct option (d)

The virial expansion for a real gas can be written in as:

$$\frac{P\overline{V}}{RT} = 1 + B_PP + C_PP^2 + \cdots \qquad \text{……(1)}$$

$$\frac{P\overline{V}}{RT} = 1 + B_VV + C_VV^2 + \cdots \qquad \text{……(2)}$$

from equation (2)

$$P = \frac{RT}{V}\left(1 + \frac{B_V}{V} + \frac{B_V}{V^2} + \cdots\right)$$

Substitute this 'P' in R.H.S of equation (1)

$$\frac{P\overline{V}}{RT} = 1 + B_P\frac{RT}{V}\left(1 + \frac{B_V}{V} + \frac{B_V}{V^2} + \cdots\right) + C_P\left\{\frac{RT}{V}\left(1 + \frac{B_V}{V} + \frac{B_V}{V^2} + \cdots\right)\right\}^2 + \cdots$$

$$\frac{\mathrm{P}\bar{\mathrm{V}}}{\mathrm{RT}} = 1 + \frac{\mathrm{B_P}RT}{\bar{V}} + \frac{1}{\bar{V}^2}\left(\mathrm{B_P B_V}RT + \mathrm{C_P}\left(RT\right)^2\right) + \cdots \qquad \text{.......(3)}$$

comparing first term on R.H.S of equation (1) and (3)

$\mathrm{B_V} = \mathrm{B_P}(RT)$;

$\mathrm{B_V} = \alpha \mathrm{B_P}$ (here $\alpha = \mathrm{RT}$)

4. Correct option (c)

since, K.E = $\frac{1}{2}\mathrm{mv}^2$

according to question,

$1\mathrm{MeV} = \frac{1}{2}\mathrm{M_\alpha S_1^2}$ ....(i)

and $2\mathrm{MeV} = \frac{1}{2}\mathrm{M_\alpha S_2^2}$ ....(ii)

dividing equation (ii) by (i)

$$\left(\frac{S_2}{S_1}\right)^2 = 2$$

$$S_2 = \sqrt{2}S_1$$

5. Correct option (c)

maxima in the curve corresponds to most probable speed of the gas

$$C_{mp} = \sqrt{\frac{2RT}{M}}$$

as $M_{Ne} < M_{Ar} < M_{Kr}$

so, ${C_{mp}}_{Ne} < {C_{mp}}_{Ar} < {C_{mp}}_{Kr}$

so, the curve C corresponds to Ne, B to Ar and A to Kr.

6. Correct option (b)

Standard deviation in speed $(\sigma_c) = \sqrt{\langle V^2\rangle - \langle V\rangle^2}$

$$= \sqrt{r_{rms}^2 - V_{avg}^2}$$

$$= \sqrt{\frac{3RT}{M} - \frac{8RT}{\pi M}}$$

$$= \sqrt{\left(3 - \frac{8}{\pi}\right)\frac{RT}{M}}$$

$$=\sqrt{\left(3-\frac{8}{\pi}\right)}\sqrt{\frac{RT}{M}}$$

$$= 0.67\sqrt{\frac{RT}{M}} \approx 0.7\sqrt{\frac{RT}{M}}$$

thus $\sigma_c \approx \sqrt{T}$

7. correct option (c)

$$V_{rms} = \sqrt{\frac{3RT}{M}} \implies V_{rms} \propto T^{1/2}$$

8. correct option (c)

$$dS = \int \frac{nC_{v,m}}{T}dT + nR\int\frac{dV}{V}$$

$$\Delta S = nC_{v,m}ln\left(\frac{T_2}{T_1}\right) + nRln\left(\frac{V_2}{V_1}\right)$$

hence, entropy is proportional to lnV

9. correct option (c)

residual entropy is given by, $S = k_B ln\, w^{N_A}$ where w is number of arrangements

Arrangements for solid OCS,

$$O = C = S$$

$$S = C = O$$

arrangements, w = 2

$S = k_B ln(2)^{N_A}$

$S = N_A k_B ln\, 2$

$S = R\ ln\, 2$

S = 8.314 × 0.693 J/K = 5.7628 J/K

10. Correct option (d)

In adiabatic process

$$\mathrm{PV}^{\gamma} = \text{constant}$$

$$P \propto \frac{1}{V^{\gamma}}$$

In isothermal process

$$\mathrm{PV} = \text{constant}$$

$$P = \frac{1}{V}$$

Since, $\gamma = 5/3$ for monoatomic gas

Thus for monoatomic gas, $P \propto \frac{1}{V^{5/3}}$

Physical Spectra

Hints & Solutions

1. CORRECT OPTION (A)

S per the B.O approximation we can consider the two different motions independent if their energy differentce is large . In other words if energy difference of two different montions is large , the coupling between them will be minimum.

In case of AX the enrgy difference vibrational and rotational energy is large compared to BX. Hence the coupling will be stronger in BX.

2. CORRECT OPTION (B)

a) THE ENTROPY OF A COMPOUND IS RELATED TO THE NUMBER OF WAYS IN WHICH THE MOLECULES CAN BE DISTRIBUTED AMONG DIFFERENT ENERGY STATES,. the greater the number ,the large is the degree of disorder ,ie, larger the entropy.

b) According to Boltzmann distr ibution, larger the energy difference wrt ground state lower will be the population in excited state.

$N_{excited}/N_{ground} = e^{-E/Kt}$; here $E=E_{ex}-E_{gs}$

Since, Ees =Bhc, so higher the value of B, lower will be the population in different excited state (ie. lower disor der or entropy)

c) $B\infty 1/1; \left[B = \frac{h^2}{8\pi^2 I}\right]$

QUANTA POINT

⇨ $B_{O2}<B_{N2}<B_{D2}<B_{H2}$
S_{ROT} for O_2 is highest.

3. CORRECT OPTION (C)

For an asymmetric top,$I_X=I_Y=I_Z$

So, Total energy (E)= $E_X+E_Y+E_Z$

$$=\frac{J_X^2}{2I_X}+\frac{J_Y^2}{2I_Y}+\frac{J_Z^2}{2I_Z} \qquad \text{[Since, E=J/2I]}$$

So, above equation will give three rotational constants B_X, B_Y and B_Z.

4. CORRECT OPTION (C)

Q- band (or PQR contour)is obtained for the bending vibration of C_2H_2 when its linearity is lost.

5. CORRECT OPTION (A)

The frequency of vibration= $\frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$

Where, k=force constant of bond

M= reduced mass

So, ratio of frequency of Co-D and Co-H bond is

$$\frac{\bar{\upsilon}_{Co-D}}{\bar{\upsilon}_{Co-H}} = \sqrt{\frac{\mu_{Co-D}}{\mu_{Co-H}}} = \sqrt{\frac{\frac{60*1}{61}}{\frac{60*2}{62}}} = \sqrt{\left(\frac{1}{2}\right)}$$

So, $\bar{\upsilon}_{Co-D} = \bar{\upsilon}_{Co-H}\sqrt{\left(\frac{1}{2}\right)} = \frac{1840}{\sqrt{2}} = 1300\ cm^{-1}$

6. Correct answer: (b)

1.The degeneracy associated with the quantum number (M_J) (the orientation of the rotation in space) is partly removed when an electric field is applied on a polar molecule (eg. HCl, NH_3 etc)

2. This splitting of states by an electric field is called Stark Effect.

3. For any linear molecule (eg. AX or BX) in electric field (E), the energy of the state with quantum number J and M_J is given by,

$$E(J,M_J) = hc\ B\times J(J+1) + a(J,M_J)\ \mu^2\ E^2$$

here energy depends on μ^2 (square of dipole moment), so large μ (dipole moment) will cause larger splitting.

$\mu_{AB} > \mu_{BX}$

7. Correct answer is (c).

From Heisenberg uncertaintity principle,

$$\Delta E\ .\Delta t\ \geq \frac{h}{4\pi} \Rightarrow\ \Delta v.\Delta t \geq \frac{h}{4\pi} \Rightarrow\ \Delta v.\Delta t \geq \frac{1}{4\pi}$$

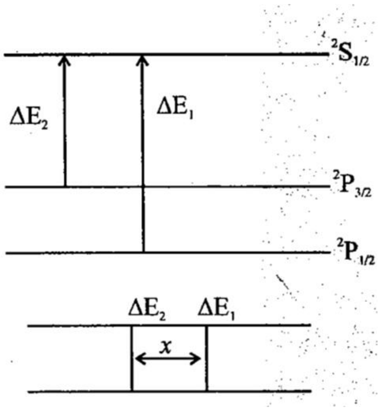
$\Delta v.\Delta t \geq$ constant …….(1)

(where $\Delta t =$ life time or Relaxation time and Δv =uncertainty in frequency)

(0.1 Hz) (1 sec) ≥ constant …..(2)

And $(\Delta \nu Hz)(10^{-4}) \geq$ constant …..(3)
From equation (2) and (3)
$0.1 \times 1 = \Delta\upsilon \times 10^{-4}$
$\Delta\upsilon = 10^3 = 1000$

8. Correct option = b



n=splitting due to spin orbital coupling $\Delta E_2 - \Delta E_1$

9. Correct answer is (a).

In AX_3 A proton spectra will be a quartet (Intensity ratio 1: 3:3:1) at δ =4.1, 4.3, 4.5 and 4.7 ppm and X proton spectra will be a doublet (Intensity ratio 1:1) J=0.2 ppm

$\frac{\Delta v \times 10^6}{v} = 0.2$ (v= 100MHz= 100×10^6 Hz)

$\frac{\Delta v \times 10^6}{100 \times 10^6} = 0.2 \Rightarrow \Delta v = 20$

10. CORRECT OPTION (B)

In Raman spectra, Stokes libes are separated by 4B cm^{-1} and have wave number value less than the incident radiation , but the first Stoke's line is observed at $\bar{\upsilon}$-6B
So, 6B= 6*2 cm^{-1}= 12 cm^{-1}.

Therefore, first Stokes line wave number = wave number of incident -12 cm^{-1} radiation
= (20487-12)cm^{-1} = 20475 cm^{-1}.

11. CORRECT OPTION (A)

$\bar{\upsilon}_{0\to1} = w_e(1 - 2x_e)$

- ⇨ 2143 cm^{-1}= $w_e - 2w_e x_e$
- ⇨ $2143 = w_e - 2 * 14$
- ⇨ $w_e = 2171\ cm^{-1}$

First overtone wave number is given by-

$$\bar{\upsilon}_{0\rightarrow 1} = w_e(1-3x_e) = 2w_e - 6w_e x_e = 2*2171 - 6*14 = 4258\ cm^{-1}$$

12. CORRECT OPTION (D)

J=0 to J=1 appears at 2B=3.9 cm^{-1}
Value of rotational constant B=3.9/2=1.95.
ΔE= 20B-12B=8B =1.95*8 =15.6 cm^{-1}.

13. CORRECT OPTION (B)

For diatomic SHO all the vibrational energy levels are equally spaced and selected rule $\Delta\bar{\upsilon}=\pm 1$ only.

14. CORRECT OPTION (C)

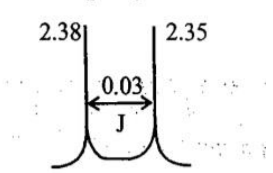
Given : w_e= 512 cm^{-1} and $w_e x_e$= 8cm^{-1}.
So, 512 *x_e= 8

⇨ X_e= 8/512

Dissociation energy $D_e = \frac{we}{4xe} = \frac{512}{\frac{4*8}{512}} = \frac{512*512}{32} = 8192\ cm^{-1}$

15. Correct option (d)

Coupling constant can be calculated as



J = (2.38-2.35)×100 $= 0.03\times 400 = 12\ Hz$

16. CORRECT OPTION(D)

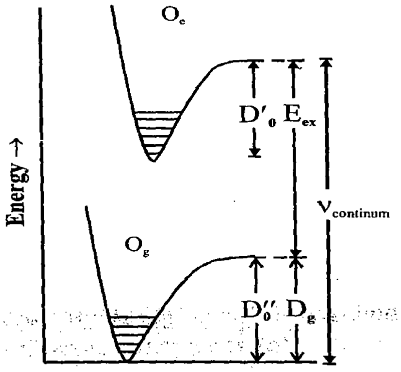


Illustration of dissociation

Dissociation energy D_g= 56875-15125 =41750 cm^{-1}.

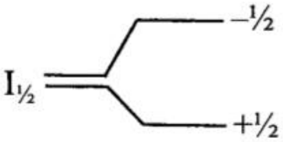
17. CO

Given : w_e= 300 cm^{-1} and x_e =0.0025
Fundamental mode=2w_e(1-3x_e)
= 300(1-2*0.0025)=300(1=0.0025)=300*0.995=298.5 cm^{-1}.
First overtone =2w_e(1-3x_e)
= 2*300(1-3*0.0025)=600(1-0.0075)=595.5 cm^{-1}.

18. Correct option (b)

Molecule contains two IR absorbtion lines and one, Raman line. So, molecule contains centre of symmetry and follow the mutual exclusion principle. Because in this type of molecule if IR band is present then Raman band absent. The common band or line is always zero. e.g. CO, type molecule.

19. Correct option (b)



$$E = -\mu \times B_0$$

$$\mu = \frac{e}{2mc} \times \frac{h}{2\pi} m_I \times g_N \quad \Rightarrow \mu_N = \frac{eh}{4\pi mc}$$

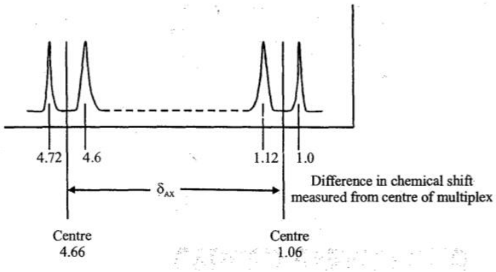
$$\mu = m_I g_n \mu_N \;\Rightarrow E = -m_I g_N \mu_N B_0 \; for\; m_I$$

$$for\; \alpha E_{mI}\left(+\frac{1}{2}\right) = -\frac{1}{2} g_N \mu_N B_0$$

$$for\; \beta E_{mI}\left(-\frac{1}{2}\right) = +\frac{1}{2} g_N \mu_N B_0$$

$$\Delta E = g_N \mu_N B_0$$

20. Correct option (a)



$$\delta_{AX} = 4.66 - 1.06 = 3.6ppm$$

Coupling constant J_{AX} is separation between peaks of a multiplet .
So, J_{AX} = 4.72- 4.6 = 1.12-1.0
= 0.12 ppm
= 0.12 x 100 = 12 Hz

21. CORRECT OPTION (B)

Since rotational patition function is given by

$$q = \frac{k_b T}{\sigma hcB} \quad where\; B = \frac{h}{8\pi^2 Ic}$$

⇨ $q = \frac{k_b T}{\sigma hc\left(\frac{h}{8\pi^2 Ic}\right)} = \frac{8\pi^2 IkT}{\sigma h^2}$

⇨ $q \propto \frac{I}{\sigma}$

Hence, 2 factors should be considered.

i) I∝μ

ii) Σ (symmetry number)

In the present case, H−C≡C−H has the smallest μ (reduced mass) also having σ=2.

Therefore, H−C≡C−H will have lowest rotational partition function.

22. Correct option (b)

F atomic mass = 19.0amu .

H atomic mass = 1 amu

H – F bond length =2 . 0 Å

$$I = \mu r^2,\ I = \frac{m_1 m_2}{m_1+m_2}\, r^2$$

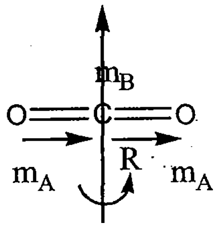
$$I = \frac{19\times 1(amu)^2}{20amu}\ \times 2.0Å\times 2.0Å = \ \frac{19}{2} amu\ \times 2.0\times 2.0\times Å^2$$

$$= \frac{19\times 1.67\times 10^{-27} kg\times 4}{20}\ \times 10^{-10}\times\ 10^{-10} m^2$$

$$\frac{76\times 1.67\times 10^{-47}}{20} kgm^2\ = 6.4\times 10^{-47} kgm^2$$

23. CORRECT OPTION (d)

The moment of inertia of CO_2.



$I=2m_AR^2$

- ⇨ $I=2*2.5*10^{-27}kg*(120pm)^2$
- ⇨ $I=2*2.5*10^{-27}kg*(120*10^{-12})^2\ m^2$
- ⇨ I=5*14400*10—51 kg m^2
- ⇨ $I=7.2*10^{-47}$ kg m^2.

24. CORRECT OPTION (C)

Homonucleur diatomic molecules does not have any permanent dipole moment. So, it will not slow rotational spectra.

On the other hand , vibration does not make changes in the permanent dipole moment of the homonucleur diatomic molecules. So, it will show the vibrational spectra. But, the homonucleu diatomic molecules shows rotational Raman and electronic spectra and with the help of both , we can calculate the bond length.'

25. CORRECT OPTION (D)

Ffor a hetero nucleur diatomic molecule non zero component of orbit angular momentum alon the molecular axis, the energy levels of the vibrational rototaional spectra will be

$E_{vib\text{-}rot}= E_{vib}+E_{rot}$

$$= BJ(J+1) + \left(v+\frac{1}{2}\right)\overline{w_e} - x_e\overline{w_e}\left(v+\frac{1}{2}\right)^2$$

Considering the transition from v=0 →v=1

ΔJ=-1 will correspond to P branch

ΔJ=0 will correspond to Q branch

ΔJ=+1 will correspond to R branch

26. CORRECT OPTION (A)

For a hetero nucleur diatomic molecule , the energy levels of the vibrational rotational spectra will be

$$E_{vib-rot} = BJ(J+1) + \left(v+\frac{1}{2}\right)\overline{w_e} - x_e\overline{w_e}\left(v+\frac{1}{2}\right)^2 \qquad \text{(in units of m}^{-1}\text{)}$$

Where, $B = \frac{h}{8\pi^2 Ic} = \frac{h}{8\pi^2 \mu r^2 c}$

Where, r= bond length of the molecule .

If the bond length of the hetero nucleur diatomic molecule is grater for upper vibrational state, the wave number corresponding to the P-branch lines will be

$$E_{vib-rot} = \overline{w_e}(1-2x_e) - [2B + J'(B-B')](J'+1)$$

Where, J'= rotational quantum number of upper vibrational state.

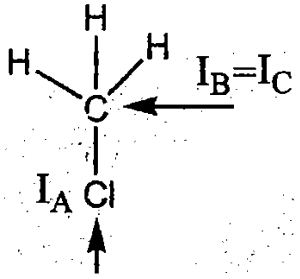
B'= rotational constant of upper vibrational state.

Gap between two successive P-branch lines is proportional to (4B-2B')

As bond length r increases, B' decreases and gap between successive absorption lines of branches increases non linearly.

27. CORRECT OPTION (B)

Symmetric rotor is CH_3Cl



Symmetric tops, $I_B=I_C\neq I_A$ where, $I_A\neq 0$

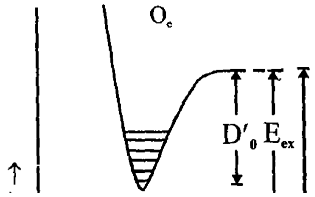
The moment of inertia about the C-Cl bond axis is now not eligible because it involves the rotation of three comparatively massive hydrogen atoms off this axis such a molecule spinning about this axis can be imagined a stop and called symmetric top.

28. CORRECT OPTION (D)

$w = \gamma B_0 = \frac{e}{2m}g$

- ⇨ $w \propto gB_0 \Rightarrow w \propto g$
- ⇨ $\frac{w_1}{w_2} = \frac{g_1}{g_2}$
- ⇨ $\frac{w_1}{700MHz} = \frac{0.4}{5.6}$
- ⇨ $w_1 = 700MHz * \frac{0.4}{5.6} = 50MHz$

29. CORRECT OPTION (B)



$\bar{\upsilon}_{\text{continuum limit}} = D_0'' + E_{ex}\ \text{cm}^{-1}$ (D_0' and D_0'' are dissociation energies).

30. CORRECT OPTION (b)

$$v = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \Rightarrow v \propto \frac{1}{\sqrt{\mu}} \quad (\mu\text{=reduced mass})$$

$$\frac{v_2}{v_1} = \sqrt{\frac{\mu_1}{\mu_2}} = \sqrt{\frac{\mu_1}{2\mu_1}} = \frac{1}{\sqrt{2}}$$

$$\Rightarrow \quad v_2 = \frac{1}{\sqrt{2}v_1}$$

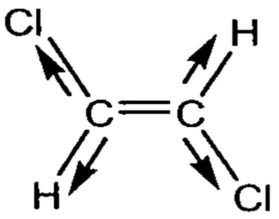
31. CORRECT OPTION (C)

$$B = \frac{h}{8\pi^2 Ic} \Rightarrow B \propto \frac{1}{I} \quad (\text{where, I=moment of inertia})$$

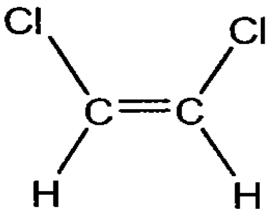
since, I for *CCl≡CF is highest.*

So, B would be the smallest for CCl≡CF.

32. CORRECT OPTION (A)



Trans -1,2-dichloroethylene dipole moment μ=0;microwave inactive.



Cis -1,2-dichloroethylene dipole moment μ≠0;microwave active.

These two compounds are distinguished on the behalf of the dipole moment by microwave spectroscopy without any calculation.

33. CORRECT OPTION(B)

$\frac{n_2}{n_1} = e^{-h\nu/(k_BT)}$

Since $\frac{n_2}{n_1} = \frac{\frac{1.n_1}{2}}{n_1} = \frac{1}{2}$ $(given)$

⇨ $\frac{1}{2} = \exp\left(-\frac{h\nu}{k_bT}\right)$ => $\ln\left(\frac{1}{2}\right) = -\frac{h\nu}{k_bT}$

⇨ $T = \frac{h\nu}{k_b ln2}$

34. Frequency (f) = $\frac{\gamma B_0}{2\pi}$

For ^{1}H $(f_H) = \frac{\gamma_H B_0}{2\pi}$ ……1

For ^{13}C $(f_c) = \frac{\gamma_c B_0}{2\pi}$ …….2

Equation 1 divided by 2

$\frac{f_H}{f_C} = \frac{\gamma_H}{\gamma_C} = \frac{42.4}{f_C} = \frac{27\times10^7}{6.75\times10^7}$

fc=$\frac{42.4MHz\times6.75}{27} = 10.6MHz$

Correct option (a)

35. CORRECT OPTION (A)

A 90^0 pulse width or pulse duration is the amount of time the pulse of energy is applied to the particular sample in order to flip all the spins into the XY plane.

The approximate field width of excitation is given by the formula ,RF_{field}= 1/(4*90^0 pulse duration in sec).

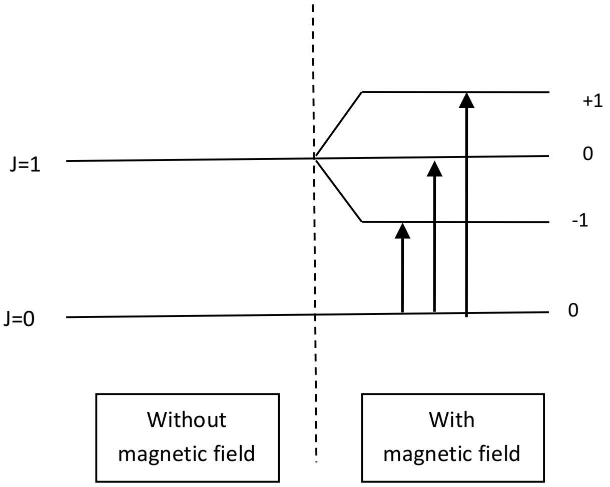
RF_{field} is the frequency associated due to the field strength =2.5*10^{-4} *42.57 MHz=10642.5 Hz.

Here, 42.57 MHz/T is gyromagnetic ratio for proton. Now, 1064.5 Hz=1/(4*pulse duration in sec)

Pulse duration=1/(1064.5*4)sec=23.5*10^{-6}sec

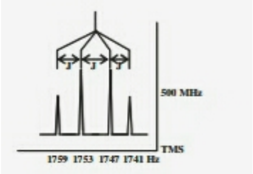
36. CORRECT OPTION (A)

Under the selection rule ,ΔM_j= 0,±1.



3 lines can be seen in the spectrum

37 Correct option is (a)



Chemical Shift **δ** = 1759+1753+1747+1741/4 = 1750 Hz /500 MHz = 3.5 ppm.

Coupling Constant J=1747-1741=6 Hz or difference between any two adjacent peaks (coupling constant is not change in Hertz).

38 Correct option is (b)

Given : V = x^2

Force = $-\frac{\partial v}{\partial x} = -\frac{\partial}{\partial x} x^2 = -2x$

V = $\frac{1}{2} K x^2 = x^2$ (given)

$\frac{1}{2} k = 1 , k = 2 = force\ constant$

39 Correct option is (b)

For allowed transition, $\Delta l = +1$ and for Lyman Series Transition is from higher level

40. Correct option is (d)

$B_{HBr} = 10\ cm^{-1}$, $\overline{v}_{HBr} = \frac{\overline{v}_{HBr}}{\sqrt{2}}$, therefore $\{ B \propto \frac{1}{\mu}\ and\ \overline{v} = \frac{2000cm^{-1}}{\sqrt{\mu}} \}$

$B_{PBr} = \frac{B_{HBr}}{2}\ and\ \overline{v}_{HBr} = \frac{\overline{v}_{HBr}}{\sqrt{2}}$

$B_{PBr} = \frac{10cm^{-1}}{2} = 5cm^{-1}\ and\ \overline{v}_{HBr} = \frac{2000cm^{-1}}{\sqrt{2}} = 1410cm^{-1}$

41. Correct option is (b)

N_2O is microwave and rotational Raman active molecule.

42. Correct option is (d)

200 MHz → 600 MHz ,J coupling constant = 10 Hz ,Difference in terms of **δ**-value remains

Constant. So, at 600MHz , 2ppm= 120 Hz .

43. Correct option is (c)

Since, due to vibrational-rotational interaction P and R lines are obtained and molecule behave as a diatomic vibrating rotor.

$$E=BJ(J+1) + \left(v+\frac{1}{2}\right)\omega_e - \left(v+\frac{1}{2}\right)^2 x_e\omega_e$$

44 Correct option is (d)

$$\frac{v_P}{v_N} = \frac{g(P)}{g(N)} = \frac{700MHz}{v_N} = \frac{5.6}{0.4} = v_N = \frac{700MHz\times0.4}{5.6} = 50MHz$$

45Correct option (b)

The first electronic absorption band maximum of a polar and relatively rigid aromatic molecule appears at 310 nm but its fluorescence maximum in acetonitrile solution appears with a large stokes shift at 450 nm. The reason for stokes shift increasing dipole moment of the molecule in the excited state.

46. Correct option is (a)

H_2 a homo diatomic molecule will have not change in dipole moment. Thus, it will be IR inactive . But since H_2 having polarisability in a Raman spectra. Thus, it will be Raman active.

47. Correct option is (b)

Only Raman active, (symmetric vibration, change in dipole moment is zero during vibration)

48. . Correct option is (c)

Spherical top molecule = CH_4 [Perfect geometry]

$I_a = I_b = I_C$.

Symmetrical top molecule ⇒CH_3CI ⇒ $I_a \neq 0,\ I_b = I_C$

49. Correct option is (c)

$$\Delta E = g\beta B_0 \ \Rightarrow hv = g\beta B_0$$

$$\Rightarrow v \propto g$$

$$\frac{v_H}{v_c} = \frac{g_H}{g_c} \Rightarrow \frac{600MHz}{v_c} = \frac{5.6}{1.4} \Rightarrow v_c = \frac{600}{4} = 150MHz$$

50 . Correct option is (a)

To make total wave function symmetric J-levels must be antisymmetric Levels with odd J will be present while levels with even J will be missing.

51. Correct option is (b)

The symmetric top molecule is allene

52. Correct option is (c)

$$\Delta E = \frac{E_{DCl}+E_{HD}}{2} - \frac{E_{HCl}+E_{D_2}}{2}$$

$$\frac{(1990+3627)}{2} - \frac{(2885+2990)}{2}\ cm^{-1}$$

$\Delta E = \frac{-258}{2}$ = -129 cm^{-1}

53. Correct option is (a)

As bond order increases, stretching frequency increases.

O_2^+= 2.5, O_2 = 2,O_2^{-1} =1.5, O_2^{-2}=1

54. Correct option is (a)

Given : 4B = 2 $cm^{-1} \Rightarrow B = 2\ cm^{-1}$

$$\frac{h}{8\pi^2\mu r^2 c} = \ 2\ cm^{-1} \Rightarrow r = \sqrt{\frac{h}{8\pi^2\mu c}}$$

$$r = \sqrt{\frac{h}{16\pi^2\mu c}}$$

55. Correct option is (a)

Reduced mass is given by $\mu = (m_1 m_2)/(m_1 + m_2)$

Here , $\mu_{HCl} = \frac{m_H m_{Cl}}{m_H + m_{Cl}}$, $\mu_{DCl} = \frac{m_D m_{Cl}}{m_D + m_{Cl}} = \frac{(2m_H)m_{Cl}}{(2m_H) + m_{Cl}}$

So, $\frac{\mu_{DCl}}{\mu_{HCl}} = \frac{(2m_H)m_{Cl}}{(2m_H) + m_{Cl}} \times \frac{m_H + m_{Cl}}{m_H m_{Cl}} = \frac{(2m_H)m_{Cl}}{(2m_H) + m_{Cl}} > 1 \Rightarrow \mu_{DCl} > \mu_{HCl}$

Vibrational frequency is given by $v = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$

Since , $\mu_{DCl} > \mu_{HCl}$, $v_{DCl} < v_{HCl}$

Zero point energy is given by $E_0 = \frac{1}{2}hv$

Since , $v_{DCl} < v_{HCl}$, therefore $(E_0)_{DCl} < (E_0)_{HCl}$

56. Correct option is (c)

$$\Delta G_{v+\frac{1}{2}} = (\varepsilon_{v+1} - \varepsilon_v) = \left(v + \frac{3}{2}\right)\omega - \left(v + \frac{3}{2}\right)^2 x_e\omega - \left(v + \frac{1}{2}\right)\omega - \left(v + \frac{1}{2}\right)^2 x_e\omega$$

$$= \omega - 2x_e\omega(v + 1)$$

Given slope = -14 $cm^{-1} = -2x_e\omega$ and intercept 2170 cm^{-1}

$$7\ cm^{-1} = x_e\omega \text{ and } \omega = 2170\ cm^{-1}$$

$$x_e = \frac{7}{2170}$$

Therefore , dissociation energy

$$\frac{\omega}{4x_e} = \frac{2170}{4\times\frac{7}{2170}} \approx 168175\ cm^{-1}$$

Dec 19

57. Correct option = 2

$\overline{v_{O-H}} = 3600\ cm^{-1}$

Since , $\overline{v} = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}} \Rightarrow \overline{v} = \frac{1}{\sqrt{\mu}}$

For O-H , $\overline{v_{O-H}} \propto \frac{1}{\sqrt{\mu_{(O-H)}}}$

And for O-D, $\overline{v_{O-D}} \propto \frac{1}{\sqrt{\mu_{(O-D)}}}$

Therefore , $\frac{\bar{v}_{O-H}}{\bar{v}_{O-D}} = \sqrt{\frac{\mu_{(O-D)}}{\mu_{(O-H)}}} = \sqrt{\frac{(16\times2)}{(16+2)}} \times \sqrt{\frac{(16+1)}{(16\times1y)}}$

$= \frac{\bar{v}_{O-H}}{\bar{v}_{O-D}} \sqrt{1.888} \Rightarrow \bar{v}_{O-D} = \frac{3600}{\sqrt{1.888}} \Rightarrow \bar{v}_{O-D} = 2620 \approx 2600 cm^{-1}$

58. Separation between two adjacent lines of Microwave (Rotational) spectrum = 2B
Therefore, 2B=4 cm^{-1}
Incident radiation (v) = 30000 cm^{-1}
First stokes lines in Rotational Raman Spectrum appears at v - 6B = 30000-12 = 29988 cm^{-1}

59. Correct option is (c)

$D_e = D_0$ +1/2hv

$D_e = D_0$ +ZPE (Zero point energy)

D_e =Depth of potential (equilibrium dissociation energy)

D_0 = Dissociation energy
$D_0 = D_e$ -ZPE (hv=0.5eV)
=4.75 eV- (0.5eV)1/2 = (4.75-0.25)eV=4.50 eV

60 . Vibrational transition energy v=0 to v=1 and v=1 to v=2

$\Delta E_{0 \to 1} = \overline{\omega_e}(1-2x_e)$ fundamental transition

$\Delta E = \overline{\omega_e}$ $(1-4x_e)$ hot band

$\overline{\omega_e}$ $(1-2x_e)$=2143.1 cm^{-1}

$\overline{\omega_e}$ $(1-4x_e)$=2116.1 cm-^{1}

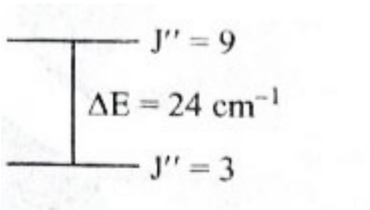
Equation (1) substract from equation (2)

$\overline{\omega_e}$ $(1-2x_e)$=2143.1 cm^{-1}

$\overline{\omega_e}$ $(1- 4x_e)$x=2116.1 cm^{-1}

$2\overline{\omega_e}xe = 27.0$ $cm^{-1} \Rightarrow \overline{\omega_e}xe = \frac{27}{2}$ cm^{-1} = 13.5cm^{-1}

61.Correct option is (b)



$E_{J''=3}$ =Bx3(3+1)=12B

$E_{J''=9}$ =Bx9(9+1)=-90B

$\Delta E =$ 90B-12B=78B

ΔE = 24 cm

$78B_{^{12}C^{16}O}$ = 24cm^{-1}

$$B_{^{12}C^{16}O} = \frac{24}{78}\text{cm} - {}^{1}\ ,\ B_{^{12}C^{16}O} \propto \frac{1}{\mu_{\cdot ^{12}C^{16}O}}\ ,\ B_{^{13}C^{16}O} \propto \frac{1}{\mu_{\cdot ^{13}C^{16}O}}$$

$$\frac{B_{^{12}C^{16}O}}{B_{^{13}C^{16}O}} = \frac{\mu_{\cdot ^{13}C^{16}O}}{\mu_{\cdot ^{12}C^{16}O}}$$

$$B_{^{13}C^{16}O} = \frac{B_{^{12}C^{16}O} \times \mu_{\cdot ^{12}C^{16}O}}{\mu_{\cdot ^{13}C^{16}O}} = \frac{24}{78} \times \frac{12\times16\times29}{28\times13\times16} = 0.29cm^{-1}$$

62. **correct answer is option c.**
Statement 1: it is wrong because, potential energy (V) ∝ q^2.
Statement 2: every option has this statement; it will definitely be correct.
Statement 3: This statement is correct, because as reduced mass increases the vibrational frequency decreases.
Statement 4: Exclude every option with (i) in it, then we get iv as wrong statement.

63. Correct option (a)
Binding energy is calculated by X-Ray Photoelectron spectroscopy (EELS (Electron energy loss spectroscopy) is the technique name).

Quadrupole splitting is an important aspect of Mossbauer Spectroscopy, caused by unsymmetrical electron filling or unsymmetrical ligand nature.

Elemental analysis is done by ESCA (Element Spectroscopy for Chemical Analysis) or EDS (both are same) involving X-Rays.

And NMR gives us chemical shift values of understudy atoms.

64. correct answer is (b)

Microwave active molecules has permanent dipole moment. So in order to check that which molecules are microwave inactive, we should see their dipole moment. Only in case of N_2 and C_2H_2 we have zero dipole moment. And to check IR activity, the molecule should have a possibility of induced dipole moment in one of its vibrational modes.

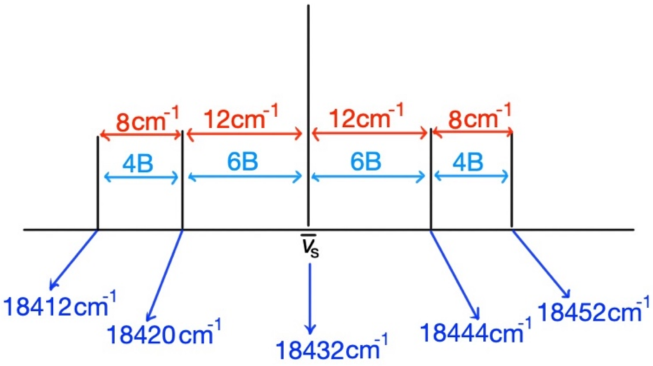
One might see this in both N_2 and C_2H_2 but the experimental fact is gases like N_2 and O_2 does not absorbs IR radiation. Hence they are inactive in IR spectroscopy.

65. **Correct option (b)**

For, Stokes line $\bar{\nu} = \bar{\nu}_{ex} - \bar{\nu}_e(1 - 2x_e)$

$\Rightarrow \ \bar{\nu} = 20000 - 1600(1 - 2\times0.01)$

$\Rightarrow \ \bar{\nu} = 18432$



12

Quantum Chemistry

Hints & Solutions

1. CORRECT ANSWER (C)

The normalized wave function for 1s orbital of H-atom is given by

$$\psi_{1s} = \frac{1}{\sqrt{\pi}}\left(\frac{1}{\alpha_0}\right)^{\frac{1}{2}} e^{-\frac{r}{\alpha_0}} \text{ and } E_{1s}=-0.5 \text{ atomic units}$$

$$\text{Since , } E_{1s} = -\frac{1}{2}\left(\frac{\varsigma^2}{n^2}\right) = -\frac{1}{2}\frac{(1.24)^2}{1} = \frac{1}{2}*1.5625 = -\frac{1}{2}*1.6 = -0.8$$

So, - 0.8 < - 0.5

2. CORRECT ANSWER (C)

A is a constant of motion (i.e, does not change with time), if

$$\frac{d}{dt} < A >= \frac{1}{i\hbar} < \left[\hat{A},\hat{H}\right] > + < \frac{\partial \hat{A}}{\partial t} >= 0$$

If $\hat{A}$ is time independent (ie, $\frac{\partial \hat{A}}{\partial t} = 0$, then for $\hat{A}$ to be constant of motion,

$\frac{1}{i\hbar} < \left[\hat{A},\hat{H}\right] >= 0 => < \left[\hat{A},\hat{H}\right] = 0$ then also we can say that A is a constant of motion

QUANTA POINT

2. CORRECT ANSWER (B)

A is a constant of motion (i.e ,does not change with time) ,if

$$\frac{d}{dt} < A > = \frac{1}{i\hbar} < [\hat{A} , \hat{H}] > + < \frac{\partial \hat{A}}{\partial t} > = 0$$

If $\widehat{A}$ is time independent (ie, $\frac{\partial \hat{A}}{\partial t} = 0$,then for $\widehat{A}$ to be constant of motion ,

$\frac{1}{i\hbar} < [\hat{A} , \hat{H}] > = 0 => < [\hat{A}, \hat{H}] = 0$, then also we can say that A is a constant of motion.

3. CORRECT OPTION (A)

Hermitian conjugate or adjoint of an operator $\widehat{A}$ is written as $\widehat{A}^\dagger$, and is defined as

$$\frac{d}{dx}^{\dagger} = -\frac{d}{dx}$$

4. CORRECT OPTION (A)

Second order perturbation for the nth state is given by

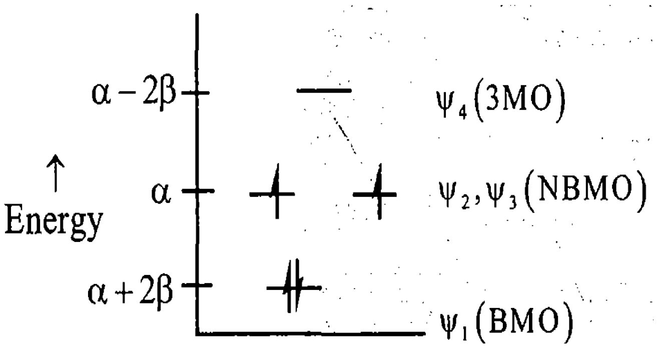
$$E_n^2 = \sum \frac{[<\Psi_m^0|H'|\Psi_n^0>]^{2}}{E_n^0 - E_m^0}$$

Therefore the perturbation for the ground state ,(ie ,n=0)

E_) ^2 = $\frac{[<\Psi_1^0|H'|\Psi_0^0>]^2}{E_0^0 - E_1^0} + \frac{[<\Psi_2^0|H'|\Psi_0^0>]}{E_0^0 - E_2^0}$

⇨ $\frac{(V_{10})^2}{E_0^0 - E_1^0} + \frac{(V_{20})^2}{E_0^0 - E_2^0} = \frac{2^2}{0-2} + \frac{4^2}{0-4} = -2 + (-4) = -6.$

5. CORECT OPTION (A)



Delocalisation energy =[2(α+2β)+2α]-4(]-4(]-4(α+β)=0.

6. CORRECT OPTION (B)

Given: Tunneling probability, $T = e^{-2kl} = e^{-10}$

Where, $k = \left(\frac{2mE}{\hbar}\right)^{\frac{1}{2}}$ and length barrier =L

If mass is halved, (m'=m/2), then

$k' = \frac{k}{\sqrt{2}}$ $and\ L' = 2L$.

So, $T = e^{-10*\left(\frac{1}{\sqrt{2}}\right)*2} = e^{-10\sqrt{2}}$.

7. CORRECT OPTION (C)

If $A^\dagger$=A, then Hermitian operator

$A^\dagger$=-A, then anti hermitian operator.

Given: $A = \frac{d}{dx} + x$

⇨ $A = -\frac{d}{dx} + x$

⇨ $A^\dagger = \left(-\frac{d}{dx}\right)^\dagger + (x)^\dagger = \frac{d}{dx} + x.$ [since, $\left(\frac{d}{dx}\right)^\dagger = -\frac{d}{dx}$ $and\ (x)^\dagger = x$

⇨ So, A is neither hermitian nor anti hermitian

$(AA^\dagger = \left[\left(\frac{d}{dx} + x\right)\left(-\frac{d}{dx} + x\right)\right]^\dagger = \left(-\frac{d}{dx} + x\right)^\dagger\left(-\frac{d}{dx} + x\right) = AA^\dagger.$

Therefore, $AA^\dagger$ is hermitian. Clearly it can be shown that $AA^\dagger$ is also hermitian.

8. CORRECT OPTION (C)

From Pauli's Exclusion Principle, " when the labels of any two identical fermions are exchanged , the total wavefunction changes sign."

As electrons are Fermions, so,

$\Psi(1,2) = \Psi(2,1)$ …..(1)

$here,$ $\Psi(1,2) = \varphi(1,2)\sigma(1,2)$

$and,$ $\Psi(2,1) = \varphi(2,1)\sigma(2,1)$ {given – $\varphi(1,2)=\varphi(2,1)$}

so, far condiiton (1), to be satisfied we must have

$\sigma(1,2)=-\sigma(2,1)$ …..(2)

the above condition satisfies only when

$\sigma(1,2) = \alpha(1)\beta(2) - \alpha(2)\beta(1)$

So, $\sigma(2,1) = \alpha(2)\beta(1) - \alpha(1)\beta(2) = -\sigma(1,2)$

9. Correct answer (b)

Given for any H-orbital

Radial function has form r^α exp[βr] and o-part has form exp[-3iϕ]. From the solution of Schrodinger equation for H-atom. We get ϕ part = $\frac{1}{\sqrt{2\pi}}e^{\pm m\phi}$, where m is integer = 0, 1, 2, 3, ……

$= \frac{1}{\sqrt{2\pi}}e^{\pm m\phi}$

(Here m can be +ve or-ve integer including zero). From given -part, m can be either +3 or-3.

Option (a)→ incorrect, $\begin{cases} for\ n > 4(let\ n = 5) \\ l > 3(let\ l = 5) \\ m = 3 \end{cases}$ {which is not possible}

Option (b)→ correct, for n = 4, l=3, m=-3 (Can be possible solution)

Option (c)→ incorrect, for n=4, l>3 (let 4), m=3

Option (d) → incorrect, for n>4, l= 3, m=-3

for n>4, I can be upto 4. (So not possible)

10. CORRECT OPTION (b)

$A^{\dagger}=A$ (Hermitian) and $A^{\dagger}=-A$(Not hermitian)

For option (A)

$\left(\frac{\hbar}{i}\frac{d}{dx}\right)^{\dagger} = \frac{\hbar}{-i}\left(-\frac{d}{dx}\right) = \frac{\hbar}{i}\frac{d}{dx}$ {since, $i^{\dagger} = -i, and \left(\frac{d}{dx}\right)^{\dagger} = -\frac{d}{dx}$ }

It is hermitian.

For option (b),$\left(i\frac{d^2}{dx^2}\right)^{\dagger} = (i)^{\dagger}\left(\frac{d}{dx}\right)^{\dagger}\left(\frac{d}{dx}\right)^{\dagger} = (-i)\left(-\frac{d}{dx}\right)\left(-\frac{d}{dx}\right) = -i\frac{d^2}{dx^2}$

So, it is not hermitian.

For option (c), $\left(\frac{d^2}{dx^2}\right)^{\dagger} = \left(\frac{d}{dx}\right)^{\dagger}\left(\frac{d}{dx}\right)^{\dagger} = \left(-\frac{d}{dx}\right)\left(-\frac{d}{dx}\right) = \frac{d^2}{dx^2}$

It is hermitian.

For option (d), $x^2 = (x)^{\dagger}(x)^{\dagger} = x.x = x^2$. so, it is hermitian.

11. CORRECT OPTION (D)

For 1-D box, the energy is

$E_n = \frac{n^2h^2}{8ml^2}$ (where, l= length of the box)

⇨ $E_n = \frac{n^2h^2}{32ma^2}$ (L=2a)

So, $E_2 = \frac{2^2h^2}{32ma^2} = \frac{4h^2}{32ma^2}$

And $E_3 = \frac{3^2h^2}{32ma^2} = \frac{9h^2}{32ma^2}$

$\Delta E = E_3 - E_2 = \frac{5h^2}{32ma^2}$.

12. CORRECT OPTION (B)

For H-atom , virial theorem,

(i) V=2E

(ii) V=-2T

(iii) T=-E

Where, E=total energy,V=potential energy,T=kinetic enerny.

So, <V>=-2<T> .

13. CORRECT OPTION (A)

Number of radial nodes= n-l-1

For s- function l=0.

Therefore, number of nodes=n-0-1=n-1

Every function either s,p,d or f have non zero at the origin.

14. CORRECT OPTION(C)

According to the Variational Principle, if any arbitrary wave function is used to calculate the energy , the value calculated is never less than the true energy.

So, energy calculated by using the trial wave functions and applying perturbation will always be greater than or equal to the true energy.

So, $(E_0^0 + E_0^1) \geq E_0$

15. CORRECT OPTION (c)

According to the Pauli's Exclusion Principle the wave function of fermions (here electrons) must be anti symmetric.(i.e., $\Psi(1,2)=-\Psi(2,1)$).

For the triplet state, spin function can be written as

$$\alpha(1)\alpha(2) or\ \beta(1)\beta(2) or\ [\alpha(1)\beta(2)+\alpha(2)\beta(1)]$$

Which are symmetric in nature. As ,$\Psi_{total}=\Psi_{space}\Psi_{spin}$, so, for Ψ_{total} to be antisymmetrical wrt electron exchange, Ψ_{space} must be antisymmetric because for the triplet state Ψ_{spin} is symmetric, so, $\Psi_{space}=\sigma_g(1)\sigma_u(2)-\sigma_u(1)\sigma_g(2)$.

16. CORRECT OPTION (D)

$(A-A^\dagger)$ is not hermitian in nature.

Because for being hermitian an operator should fulfill the condition that $(OP)^\dagger=(OP)$

$(A-A^\dagger)^\dagger=A^\dagger-A=-(A-A^\dagger)$.

So, it is anti hermitian in nature.

17. CORRECT OPTION (D)

As we know that , the energy of hydrogen like atom with nucleur charge ‘z’ the enrgy of orbital with the principal quantum number (n) is

$E = -\frac{13.6Z^2}{n^2} \;=> E_n \propto -\frac{Z^2}{n^2}$

18. CORRECT OTPION (B)

The average value of radius <r> in the is stat eof hydrogen atom is

$$< r > = \int \Psi_{1s}^{*} \hat{r} \Psi_{1s} d\tau = \int_0^{\infty} \frac{1}{\sqrt{\pi}\, a_0^{\frac{3}{2}}} \hat{r} \frac{1}{\sqrt{\pi}\, a_0^{\frac{3}{2}}} \; e^{-\frac{r}{a_0}} 4\pi r^2 dr$$

$$= \frac{4}{a_0^3} \int_0^{\infty} r^3 e^{-\frac{2r}{a_0}} dr = \frac{4}{a_0^3} \frac{3!}{\left(\frac{2}{a_0}\right)^4} = \frac{24a_0}{16} = \frac{3}{2} a_0$$

19. CORRECT OPTION (B)

Given: $\Psi = \sqrt{\frac{2}{\mathrm{l}}} \sin \frac{n\pi x}{l}$

Probability P=$\int \Psi^{*}\Psi \; d\tau$

⇨ $\int_{l/4}^{3l/4} \sqrt{\frac{2}{\mathrm{l}}} \sin \frac{n\pi x}{l} \sqrt{\frac{2}{\mathrm{l}}} \sin \frac{n\pi x}{l} \; dx$

⇨ $\frac{2}{l} \int_{\frac{l}{4}}^{\frac{3l}{4}} \sin^2 \frac{n\pi x}{l} \; dx \quad => \frac{n\pi}{l} = a$

⇨ $\frac{2}{l} \int_{\frac{l}{4}}^{\frac{3l}{4}} sin2ax \; dx => \frac{2}{l} \int_{\frac{l}{4}}^{\frac{3l}{4}} \frac{[1-cos2ax]}{2} \; dx$

⇨ $\frac{2}{2l} \left[\int_{\frac{l}{4}}^{\frac{3l}{4}} 1dx - \int_{\frac{l}{4}}^{\frac{3l}{4}} \cos 2ax \; dx \right]$

⇨ $\frac{1}{l} \left[[x]_{\frac{l}{4}}^{\frac{3l}{4}} - \left[\frac{sin2ax}{2a}\right]_{\frac{l}{4}}^{\frac{3l}{4}} \right]$

⇨ $\frac{1}{l}\left[\left(\frac{3l}{4} - \frac{l}{4}\right) - \frac{1}{2a}\left(sin2a\frac{3l}{4} - sin2a\frac{l}{4}\right)\right] = \frac{1}{l}\left[\frac{l}{4} - \frac{1}{2a}\left(\sin\frac{3al}{2} - \sin\frac{al}{2}\right)\right]$

⇨ $\frac{1}{l}\left[\frac{l}{2} - \frac{1}{2a}\left(\sin\frac{3n\pi l}{2l} - \sin\frac{n\pi l}{2l}\right)\right]$ (n=1)

⇨ $\frac{1}{l}\left[\frac{l}{2} - \frac{1}{2a}\left(\sin\frac{3\pi}{2} - \sin\frac{\pi}{2}\right)\right]$

⇨ $\frac{1}{l}\left[\frac{l}{2} - \frac{1}{2a}(-1-1)\right]$

⇨ $\frac{1}{l}\left(\frac{l}{2} - \frac{1}{2\mathrm{a}}(-2)\right)$

- ⇨ $\frac{1}{l}\left[\frac{l}{2}-\frac{1}{\frac{n\pi}{l}}(-2)\right]$
- ⇨ $\frac{1}{l}*\frac{l}{2}+\frac{1}{l}*\frac{l}{n\pi}=\frac{1}{2}+\frac{1}{\pi}$
- ⇨ Probability $=\frac{1}{2}+\frac{1}{\pi}$

20. CORECT OPTION (C)

Particle in a 3D cubic box of length L has energy of $\frac{14h^2}{8mL^2}$.

The degeneracy may be calculated by taking the energy formula for3D cubic box into consideration: $\frac{n_x^2+n_y^2+n_z^2}{8ml^2}=\frac{14h^2}{8ml^2}$

So, $n_x^2+n_y^2+n_z^2=14$.

n_x, n_y,n_z combination may be (1,2,3)(1,3,2)(2,1,3)(3,1,2)(3,2,1)

At the energy level $\frac{14h^2}{8ml^2}$,there is 6 energy states, so, degeneracy=6.

21. CORRECT OPTION (B)

Energy correction for second order energy

$$E_n^2=\sum_{m\neq n}\frac{<\varphi_m|\widehat{w}|\varphi_n>}{E_n^0-E_m^0}$$

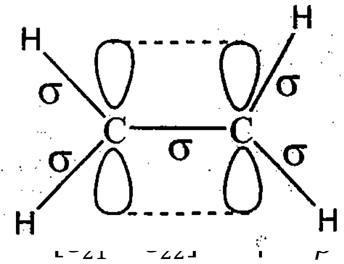
Generally, $E_n^0<E_m^0$

So, second order correction to energy is negative.

So, statement (a) and (b) is true.

22. CORRECT OPTION (C)

$H_2C=CH_2$



The secular determ

$$\begin{matrix}\beta\\ \alpha-E\end{matrix}\Bigg|=0$$

Dividing each element of the aboe determinant by β and then setting (α-E)/β =x. we get,

$$\begin{vmatrix}x & 1\\ 1 & x\end{vmatrix}=0$$

Which on expanding gives,

$x^2-1=0$

The two roots of the above equation ,x=1 and x=-1
Thus, α-E/β =-1 or (α-E)/β=1
Which gives : $E_+ = \alpha+\beta$ and $E_- = \alpha-\beta$

23. CORRECT OPTION (D)

For the molecule H_2 in the excited state $\sigma_g^1\sigma_s^1$. The spin part of triplet state with m_s , is proportion to,

$$\text{The three triplet states}\begin{cases} \alpha(1)\alpha(2) & m_s = +1 \\ \frac{1}{\sqrt{2}}[\alpha(1)\beta(2)+\beta(1)\alpha(2)] & m_s = 0 \\ \beta(1)\beta(2) & m_s = -1 \end{cases}$$

So, the triplet state with m_s =0 is $\frac{1}{\sqrt{2}}[\alpha(1)\beta(2)+\beta(1)\alpha(2)]$

24. CORRECT OPTION (C)

The eigen values of an anti hermitian operator are either purely imaginary or equal to zero. If A and B are non commuting hermitian operator. So, all Eigen values are purely imaginary or zero.

25. COORECT OPTION (D)

The value of $[x, p_x^n] = ni\hbar p_x^{n-1}$
$\therefore [x, p_x^2] = 2i\hbar p_x$

26. CORECT OPTION (C)

Combining the two real wave function φ_1 and φ_2 constructed functions $(\varphi_1+\varphi_2)$ and $i(\varphi_1+\varphi_2)$ represent the same state because if these two functions multiplied by any constant , no effect on the state and on the energy because multiply only in the eigen value , no effect on the energy and no effect on the wave function. If we use any eigen function which gives eigen value, if multiply by any constant no change in the eigen function and no change in the energy of the state. Energy is same,so, state is same only change in eigen value.

27. CORRECT OPTION (A)

$$\begin{vmatrix} H_{11}-ES_{11} & H_{12}-ES_{12} \\ H_{21}-ES_{21} & H_{22}-ES_{22} \end{vmatrix} \qquad S_{11}=1; S_{22}=1; S_{12}=S_{21}=0$$

$H_{11} =< \varphi_1|H|\varphi_1 > = 0; H_{21} = H_{12} =< \varphi_1|H|\varphi_2 > =< \varphi_2|H|\varphi_1 > = 2.0$
$H_{22} =< \varphi_2|H|\varphi_2 >= 3.0$

$$\begin{bmatrix} 0-E & 2-0 \\ 2-0 & 3-E \end{bmatrix} = -3E + E^2 - 4 = 0$$

⇨ $E^2 - 3E - 4 = 0$

⇨ $E^2 - 4E + E - 4 = 0$

⇨ $E(E-4) + 1(E-4) = 0$

⇨ $(E-4)(E+1) = 0$

⇨ E=4 or -1.

Ground state is lower energy =-1.

28. CORRECT OPTION (D)

Polar molecule AB →A^+B^- has the form $C_A\Psi_A + C_B\Psi_B$

$C_A^2 + C_B^2 = 1$ for normalization.

Probability o atom B find the electron =90%

C_B^2=90%=0.9 =>C_B^2=0.9

C_B^2=0.9 and C_A^2=0.1

$C_B = \sqrt{0.9} = 0.95$; $C_A = \sqrt{0.1} = 0.32$

29. Correct answer is (c)

For harmonic oscillator, the ground stationary state wave function is ,

$given : \psi_0 = exp[-Ax^2]$

Compare equation (1) and (2) , we get

$A = \frac{\beta}{2} = \beta = 2A \quad \left[\beta = \frac{\sqrt{mk}}{\mathrm{h}}\right]$

$\frac{\sqrt{mk}}{\mathrm{h}} = 2A \Rightarrow A = \frac{\sqrt{mk}}{2\mathrm{h}} \Rightarrow [\mathrm{A} \propto k^{\frac{1}{2}}]$

30. Correct answer is (a)

The energy of a harmonic oscillator in its ground state is $1/2h\omega$

According to Virial Theorem for SHO

Every contribution is equal for kinetic energy operator and potential energy operator.

E = K+V

E = K+K. (K=V)

E = 2K. (E=hω)

$\frac{\mathrm{h}\omega}{2} = \mathrm{k}$

$\left[\frac{\mathrm{h}\omega}{2} = 2k \Rightarrow k = \frac{\mathrm{h}\omega}{4}\right]$

Energy $\frac{\mathrm{h}\omega}{2}$ only possible if k =$\frac{\mathrm{h}\omega}{4}$ and V=$\frac{\mathrm{h}\omega}{4}$energy contribution is equal for K and V.

31. Correct answer is (c)

Energy of a hydrogen in a state is $\frac{-h_c R_H}{n^2}$ $\left[-13.6\frac{z^2}{n^2}\right]$

Degeneracy $g_n = n^2$. (for hydrogen atom)
If spin include = $2n^2$ Given: $\frac{-h_c R_H}{25}$
Compare with equation (1), $n^2 = 25$
Degeneracy = 25

32. Correct answer is (a)

In many electron atom, there is strong electron-election i.e. inter-electron repulsion. Due to inter electron repulsion, the orbital angular momentum (I_1 , I_2) as well as spin angular momenta (s_1 , s_2) are coupled together to give total orbital angular momentum (L) and spin (S).

33. CORRCET ANSWER (D)

n=2 → n=1

energy of 1-D box, $E_n = \frac{n^2h^2}{8ml^2}$

⇨ $\frac{2^2h^2}{8ml^2} \rightarrow \frac{1^2h^2}{8ml^2}$

So, $\Delta E = \frac{3h^2}{8ml^2} = 6\ unit(given) => \frac{h^2}{8ml^2} = \frac{6}{3} = 2units$ …..(1)

n=3→n=2 (difference)

for , $\frac{3^2h^2}{8ml^2} \rightarrow \frac{2^2h^2}{8ml^2}$ $=> \Delta E = 5\times\frac{h^2}{8ml^2}$

$\Delta E=5\times2=10$ unit.

34. CORRECT ANSWER (c)

$\Psi = \sqrt{\frac{1}{4}}\Psi_1 + \sqrt{\frac{3}{4}}\Psi_2$ ….(1)

$\Psi = c_1\Psi_1 + c_2\Psi_2$ ….(2)

From the equation (1) and (2) , we get,

$c_1 = \sqrt{\frac{1}{4}}\ and\ c_2 = \sqrt{\frac{3}{4}}$ (since probability)

Probability corresponding E_1 equal to c_1^2 ,

$c_1 = \sqrt{\frac{1}{4}} => c_1^2 = \frac{1}{4}$

35. CORRECT ANSWER (B)

As we know for the particle in 1-D box

$E_n = \frac{n^2h^2}{8ml^2}$

Variational principle says,

$E_{approx} > E_{actual}$

$\Psi_{approx} = x\left(\frac{l}{2} - x\right)(l - x)$

$\left.\begin{array}{l} at\ x = 0, \Psi = 0 \\ at\ x = l,\ \ \Psi = 0 \end{array}\right\} boundary\ condition$

Also, at $x = \frac{l}{2} \quad \Psi = 0\Big\} node\ means\ given\ wave\ function\ represent\ n = 2\ , one\ node$

So, $E_{approx} > \frac{n^2h^2}{8ml^2}$

$E_{approx} > \frac{h^2}{2ml^2} \; => E_{approx} > \frac{2^2h^2}{8ml^2}$.

36. CORRECT OPTION (C)

In $r^2(\alpha_1 - r)(\alpha_2 - r)e^{-\beta r}$,

Where, $(\alpha_1 - r)$ = represent one radial node i.e., α_1=r

$(\alpha_2 - r)$ = represent one radial node i.e., α_2=r

i.e., 2 total nodes.

We know that , radial node =n-l-1=2

For option (c), n=5,l=2

Radial node =5-2-1=2

37. CORRECT OPTION (C)

Operator $[x, [x, p^2]]$

$[x, 2i\hbar p] = 2i^2\hbar^2 \quad ; \quad [x, p^2] = 2i\hbar p \quad ; because\ [x, p_x^n] = ni\hbar p_x^{n-1}$

$\Rightarrow -[p[x^2, p]] \Rightarrow -[p, 2i\hbar x] \Rightarrow \; -2i\hbar[p, x] \Rightarrow -2i\hbar(-i\hbar) = 2i^2\hbar^2$

38. CORRECT OPTION (C)

$\int_0^L \Psi < x^3 > \Psi^* d\tau$

⇨ $\int_0^L \sqrt{\frac{2}{l}} \sin\frac{n\pi x}{l}\ x^3\ \sqrt{\frac{2}{l}} \sin\frac{n\pi x}{l}\ dx$

⇨ $\frac{2}{L}\int_0^L x^3 \sin^2\frac{n\pi x}{l}$

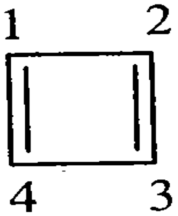
⇨ $\frac{2}{L}\ \int_0^L \frac{x^3\left(1 - \cos\frac{2n\pi x}{l}\right)}{2} dx$

⇨ $\frac{2}{L}\left[\int_0^L \frac{x^3}{2} dx - \frac{1}{2}\int_0^L x^3 \cos\frac{2n\pi x}{l} dx\right]$

⇨ $\frac{2}{L}\frac{1}{2}\left[\frac{x^4}{4}\right]_0^L$

⇨ $\frac{L^3}{4}$

39. CORRECT OPTION (C)



$$\begin{bmatrix} H_{11}-ES_{11} & H_{12}-ES_{12} & H_{13}-ES_{13} & H_{14}-ES_{14} \\ H_{21}-ES_{21} & H_{22}-ES_{22} & H_{23}-ES_{23} & H_{24}-ES_{24} \\ H_{31}-ES_{31} & H_{32}-ES_{32} & H_{33}-ES_{33} & H_{34}-ES_{34} \\ H_{41}-ES_{41} & H_{42}-ES_{42} & H_{43}-ES_{43} & H_{44}-ES_{44} \end{bmatrix}$$

$H_{11} = H_{22} = H_{33} = H_{44} = \alpha \quad (COULUMB\ INTEGRAL)$

$H_{12} = H_{21} = H_{14} = H_{41} = H_{23} = H_{32} = H_{34} = H_{43} = \beta \quad (EXCHANGE\ INTEGRAL\ )$

$H_{13} = H_{31} = H_{24} = H_{42} = 0$

$$\begin{cases} S_{11} = S_{22} = S_{33} = S_{44} = 1 \\ S_{12} = S_{21} = S_{32} = S_{13} \dots = 0 \end{cases} \quad (OVERLAP\ INTEGRAL)$$

$$\begin{bmatrix} \alpha-E & \beta & 0 & \beta \\ \beta & \alpha-E & \beta & 0 \\ 0 & \beta & \alpha-E & \beta \\ \beta & 0 & \beta & \alpha-E \end{bmatrix}$$

40. CORRECT OPTION (D)

In molecular orbital treatment of H_2 , two electrons with opposite spins are assigned to the lowest molecular orbital Ψ_+. Thus , the spatial wave function of H_2 is

$\Psi_{spatial} = \Psi_+(1)\Psi_+(2) = \frac{1}{2(1+s)}\{\Psi_{1s(H_a)}(1) + \Psi_{1s(H_b)}(1)\}\{\Psi_{1s(H_a)}(2) + \Psi_{1s(H_b)}(2)\}$

Opening out the above expression, we get,

$\Psi_{spatial} = \frac{1}{2(1+s)}\ [\ \Psi_{1s(H_a)}(1)\Psi_{1s(H_a)}(2) + \Psi_{1s(H_a)}(1)\Psi_{1s(H_b)}(2) + \Psi_{1s(H_b)}(1)\Psi_{1s(H_a)}(2) + \Psi_{1s(H_b)}(1) + \Psi_{1s(H_b)}(2)$

In the above expression, the various terms represent structures as described below:

First and fourth terms: the terms are $\Psi_{1s(H_a)}(1)\Psi_{1s(H_a)}(2)$ and $\Psi_{1s(H_b)}(1) + \Psi_{1s(H_b)}(2)$. These configurations assign both the electrons either to atom H_a or H_b and hence they represent ionic structures.

Second and third terms: the terms are $\Psi_{1s(H_a)}(1)\Psi_{1s(H_b)}(2)\ and\ \ \Psi_{1s(H_b)}(1)\Psi_{1s(H_a)}(2)$. These configurations assign one electron to each of the atom and hence they represent covalent structures. Since, the coefficients of all the terms are identical; it follows MO treatment gives equal weightage to the ionic and covalent structures. It is expected that the MO function will be poor at large internucleur separations since the dissociation products will be an equal mixture of ions and distances one expects that there will also be some chance of finding both electrons in the same atomic orbitals. Thus, MO treatment does take into account this fact, but perhaps gives more weightage to this fact than what actually exists in the molecule.

41. CORRECT OPTION (B)

For radial nodes –n-l-1=5-2-1=2

Angular nodes=l=2

42. CORRECT OPTION (C)

$$V(x,y) = \frac{1}{2}k_x x^2 + \frac{1}{2}k_y y^2 = V(x) + V(y)$$

$$-\frac{\hbar^2}{2m}\left(\frac{d^2}{dx^2} + \frac{d^2}{dy^2}\right)\Psi(x,y) + \big(V(x) + V(y)\big)\Psi(x,y) = E\Psi(x,y)$$

$$\Psi(x,y) = \Psi(x)\Psi(y) => -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\Psi(x) + V(x)V(y) = E\Psi(x,y)$$

⇨ $$-\frac{\hbar^2}{2m}\left\{\frac{\Psi(x)\frac{\partial^2\Psi(x)}{\partial x^2}}{\Psi(x)\Psi(y)} + \frac{\Psi(x)\frac{\partial^2\Psi(x)}{\partial y^2}}{\Psi(x)\Psi(y)} + \big(V(x) + V(y)\Psi(x,y) = E\Psi(x,y)\big)\right\}$$

⇨ $$-\frac{\hbar^2}{2m}\left[\frac{1}{\Psi(x)}\frac{\partial^2}{\partial x^2}\ \Psi(x) + \frac{1}{\Psi(y)}\frac{\partial^2}{\partial y^2}\ \Psi(y) + V(x)V(y)\Psi(x,y) = E\Psi(x,y)\right]$$

⇨ $$-\frac{\hbar^2}{2m}\frac{1}{\Psi(x)}\frac{\partial^2}{\partial x^2}\Psi(x) + V(x) = E + \frac{\hbar^2}{2m}\frac{1}{\Psi(y)}\frac{\partial^2}{\partial y^2}\ \Psi(y)$$

Since, $E = KE + PE = \frac{P_X^2}{2m} + \frac{P_y^2}{2m} + V(x) + V(y) = \left[\frac{P_x^2}{2m} + \frac{P_y^2}{2m} + V(x) + V(y)\right]$

$$= \left[\frac{P_x^2}{2m} + V(x)\right] + \left[\frac{P_y^2}{2m} + V(y)\right]$$

∴$E=E_X+E_Y$.

43. CORRECT OPTION (A)

$$V(x,y,z) =< x\frac{\partial V}{\partial x} + y\frac{\partial V}{\partial y} + z\frac{\partial V}{\partial z} > = 2 \qquad .....(1)$$

$$V(x) = \frac{1}{2}k_x x^2\ ; V(y) = \frac{1}{2}k_y y^2\ \ ;\ \ V(z) = \frac{1}{2}\ k_z z^2$$

$$\frac{\partial V}{\partial x} = 2 * \frac{k_x x}{2} = k_x x\ ;\ \frac{\partial V}{\partial y} = 2 * \frac{k_y y}{2} = k_y y\ ;\ \frac{\partial V}{\partial z} = 2 * \frac{k_z z}{2} = k_z z$$

Put these in equation (1)

$$< xk_X + yk_y + zk_z > = 2T$$

$$< k_x x^2 + k_y y^2 + k_z z^2 > = 2T$$

$$2 < V >= 2 < T > => < V > = < T >$$

44. CORRECT OPTION (D)

Particle in a box Hamiltonian as zeroth order Hamiltonian and potential v_i from a/2 to a.

$\int_{a/2}^{a}\sqrt{\frac{2}{a}}\sin\frac{n\pi x}{a}\ V_1\sqrt{\frac{2}{a}}\sin\frac{n\pi x}{a}\ dx$

⇨ $\int_{a/2}^{a}\frac{2}{a}\ V_1\sin^2\frac{n\pi x}{a}dx$

⇨ $\frac{2}{a}V_1\int_{a/2}^{a}\sin^2\frac{n\pi x}{a}dx$

⇨ $\frac{2}{a}V_1\int_{a/2}^{a}\frac{1-\cos\frac{2n\pi x}{a}}{2}dx$

⇨ $\frac{2}{a}V_1 * \frac{1}{2}\left[\int_{\frac{a}{2}}^{a}1dx - \int_{\frac{a}{2}}^{a}\cos\frac{2n\pi x}{a}dx\right]$

⇨ $\frac{2}{a}V_1\frac{1}{2}\left[[x]_{\frac{a}{2}}^{a} - \frac{a}{2n\pi}\left[\sin\frac{2n\pi x}{a}\right]_{\frac{a}{2}}^{a}\right]$

⇨ $\frac{2}{a}V_1\frac{1}{2}\left\{\left[a-\frac{a}{2}\right] - \frac{a}{2n\pi}\ [\sin 2n\pi - \sin n\pi]\right\}$

⇨ $since, \sin n\pi = 0, \sin 2n\pi = 0$

⇨ $\frac{2}{a}V_1\frac{1}{2}\left[\frac{a}{2} - \frac{a}{2n\pi}\ [0-0]\right]$

⇨ $\frac{2}{a}V_1\frac{1}{2}\left[\frac{a}{2}\right] = \frac{V_1}{2}$

$\therefore E = \frac{n^2h^2}{8\pi a^2} + \frac{V_1}{2}\ \ (perturbed\ part\ )$

45. CORRECT OPTION (B)

$\Psi = \frac{1}{\sqrt{\pi}a_0^{\frac{3}{2}}}e^{-\frac{r}{a_0}}$

$P(r)dr = \int_0^\infty \Psi_{1s}\Psi_{1s}^*\,d\tau\quad [d\tau = 4\pi r^2]$

$P(r)dr = \int_0^\infty \frac{1}{\sqrt{\pi}a_0^{\frac{3}{2}}}e^{-\frac{r}{a_0}}\frac{1}{\sqrt{\pi}a_0^{\frac{3}{2}}}e^{-\frac{r}{a_0}}4\pi r^2\ dr$

⇨ $P(r)dr = 4\pi r^2|\Psi_{1s}|^2dr$

⇨ $P(r)dr = 4\pi r^2\frac{1}{\pi a_0^3}e^{-\frac{2r}{a_0}}dr$

Most probable distance ,$\frac{dP(r)}{dr} = 0$

⇨ $\frac{dP(r)}{dr} = \frac{4}{a_0^3}\frac{d}{dr}\left(r^2e^{-\frac{2r}{a_0}}\right) = 0$

⇨ $\frac{4}{a_0^3}\left[-\frac{2r^2}{a_0}\ e^{-\frac{2r}{a_0}} + e^{-\frac{2r}{a_0}}2r\ \right] = 0$

⇨ $\frac{4}{a_0^3}\ 2r\ e^{\frac{2r}{a_0}}\left[-\frac{r}{a_0}+1\right] = 0$

⇨ $-\frac{r}{a_0}+1 = 0$

⇨ $\frac{r}{a_0} = 1$

⇨ $r = a_0$

46. CORRECT OPTION (B)

$L = L_x\hat{\imath} + L_y\hat{\jmath} + L_z\hat{k}$

Since, L=mvr →P

And $r = x\hat{\imath} + y\hat{\jmath} + z\hat{k}$; $P = p_x\hat{\imath} + p_y\hat{\jmath} + p_z\hat{k}$

$L = \vec{r}\ X\ \vec{P}$

$$\begin{bmatrix} \hat{\imath} & \hat{\jmath} & \hat{k} \\ x & y & z \\ p_x & p_y & p_z \end{bmatrix} = \hat{\imath}(yp_z - zp_y) - \hat{\jmath}(xp_z - p_X z) + \hat{k}(xp_y - p_X y)$$

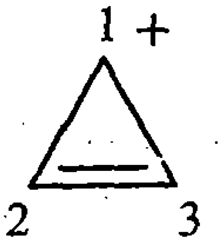
$L = L_x\hat{\imath} + L_y\hat{\jmath} + L_z\hat{k} = \hat{\imath}(yp_z - zp_y) - \hat{\jmath}(xp_z - p_X z) + \hat{k}(xp_y - p_X y)$

$L_X = \hat{\imath}(yp_z - zp_y)$; $L_y = -(xp_z - p_X z)$; $L_z = (xp_y - p_X y)$

$p_x = -i\hbar\frac{d}{dx}$; $p_z = -i\hbar\frac{d}{dz}$

$$L_y = z\left(-i\hbar\frac{d}{dx}\right) - x\left(-i\hbar\frac{d}{dz}\right) = -i\hbar\left[z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right] = -\frac{i^2}{i}\hbar\left[z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right] = \frac{\hbar}{i}\left[z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right]$$

47. CORRECT OPTION (C)



Huckel determinant

$$\begin{bmatrix} C_{11} & C_{12} & C_{13} \\ C_{21} & C_{22} & C_{23} \\ C_{31} & C_{32} & C_{33} \end{bmatrix} \equiv \begin{vmatrix} \alpha - E & \beta & \beta \\ \beta & \alpha - E & \beta \\ \beta & \beta & \alpha - E \end{vmatrix} = 0$$

LET $x = \frac{\alpha - E}{\beta}$ …..(1)

$$\begin{vmatrix} x & 1 & 1 \\ 1 & x & 1 \\ 1 & x & 1 \end{vmatrix} = 0 => x\begin{vmatrix} x & 1 \\ 1 & x \end{vmatrix} - 1\begin{vmatrix} 1 & 1 \\ 1 & x \end{vmatrix} + 1\begin{vmatrix} 1 & x \\ 1 & 1 \end{vmatrix} = 0$$

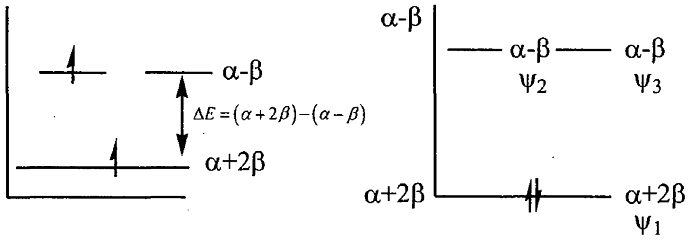
- ⇨ $x(x^2 - 1) - 1(x - 1) + 1(1 - x) = 0$
- ⇨ $x^3 - x - x + 1 + 1 - x = 0$
- ⇨ $x^3 - 3x + 2 = 0$
- ⇨ $(x + 2)(x - 1)^2 = 0$
- ⇨ $(x + 2)(x - 1)(x - 1) = 0$
- ⇨ $x = -2,1,1$

For x=-2, so from eq. (1)

$\frac{\alpha - E}{\beta} = -2 => E = \alpha + 2\beta$

For x=1,so from eq(1): $\frac{\alpha - E}{\beta} = 1 => E = \alpha - \beta$

Single electron excitation in cyclopropenium cation



$\Delta E = (\alpha - 2\beta) - (\alpha - \beta) = 3\beta$.

48. CORRECT OPTION(C)

$[\widehat{T_x}, \widehat{p_x}]\Psi$

⇨ $\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}, -i\hbar\frac{\partial}{\partial x}\right]\Psi$

⇨ $-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\frac{\partial \Psi}{\partial x} - \frac{i\hbar\hbar^2}{2m}\frac{\partial}{\partial x}\frac{\partial}{\partial x}\frac{\partial \Psi}{\partial x}$

⇨ $\frac{\hbar^2 i\hbar}{2m}\frac{\partial^3 \Psi}{\partial x^3} - \frac{i\hbar^2\hbar}{2m}\frac{\partial^3 \Psi}{\partial x^3}$

⇨ $\frac{\hbar^3 i\hbar}{2m}\frac{\partial^3 \Psi}{\partial x^3} - \frac{\hbar^3 i\hbar}{2m}\frac{\partial^3 \Psi}{\partial x^3} = 0$

49. CORRECT OPTION(A)

For cubic box

Energy = $E = \frac{h^2}{8ml^2}(n_x^2 + n_y^2 + n_z^2)$ …(1)

For cubic box lowest energy

$E(lowest) = \frac{3h^2}{8ml^2}$

If energy is twice, $E = 2 * \frac{3h^2}{8ml^2} = \frac{6h^2}{8ml^2}$ …(2)

From eq.(1) and (2),we get,

$n_x^2 + n_y^2 + n_z^2 = 6$

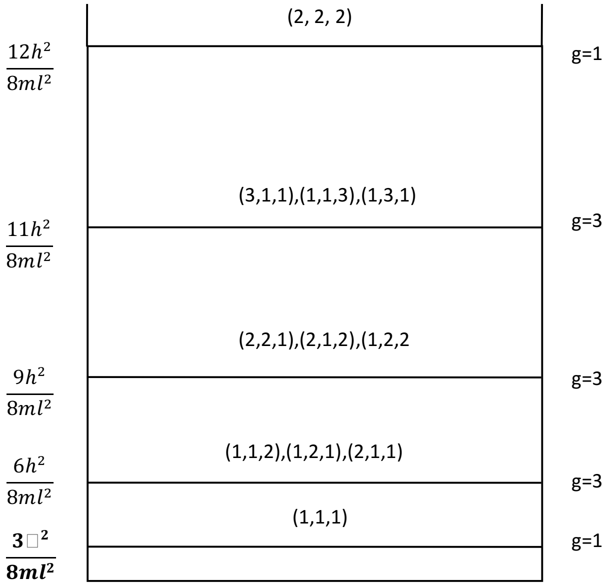
It follows if

$n_x = 1, n_y = 1, n_z = 2$

Or $n_x = 2, n_y = 1, n_z = 1$

Or, $n_x = 1, n_y = 2, n_z = 1$

So, it gives 3 degenerate levels (g=3).



50. CORRECT OPTION (B)

When the variational terms are increased the energy come closer to the ground state energy. So, the energy of two even function x(x-a) and $x^2(x-a)^2$ correspond to the energy E_2 come closer to E_0 because the system are very complicated and not solve easily.

51. CORRECT OPTION (A)

For the hydrogen atom,

Virial Theorem :2<T>=-<V> .

$2 < kinetic\ energy > = - < potential\ enrgy >$

$Ground\ state\ energy = -13.6eV$

Since, $2 < kinetic\ energy > = - < potential\ enrgy >$

<Potential energy>=-2*13.6= -27.2

<Kinetic energy>= 13.6

52. CORRECT ANSWER(B)

$c_1^2 + c_2^2 + 2c_1c_2s = 1$

$(0.8)^2 + (0.4)^2 + 2 * 0.4 * 0.8 * s = 1$

⇨ $0.64 + 0.16 + 0.64s = 1$

⇨ $0.64s = 1 - 0.80$

⇨ $0.64s = 0.20$

⇨ $s = \frac{0.2}{0.64} = 0.31$

53. Correct answer is (c)

The formula for ionisation energy is

I.E= $\frac{13.6 \times z^2\ eV}{n^2}$ / [z= atomic number, n = shell number]

This is for one electron 'H' atom like system

Hence, for Li^{++} = 1s1 (one electron system)

LE. = $\frac{13.6 \times 3^2\ eV}{1^2}$= 13.6×9. For 'H' atom, I.E. = LE.= $\frac{13.6 \times 1^2\ eV}{1^2}$=13.6 =x

Therefore, I.E. of Li^{++} = 9x

54. Correct answer is (c)

In simple Hückel molecular orbital theory only distinguishes between cis-butadiene and cyclobutadiene on the bases of energy correction. In cyclobutadiene delocalization energy is zero and cis butadiene is 0.4728β

55. Correct answer is (a)

$$\int_{-\infty}^{\infty}\left(\frac{\beta}{\pi}\right)^{1/4} e^{\frac{-\beta x^2}{2}}dx$$

$$\left(\frac{\beta}{\pi}\right)^{1/2}\int_{-\infty}^{+\infty} \lambda x e^{-\beta x^2}dx \Rightarrow \left(\frac{\beta}{\pi}\right)^{1/2}\lambda\int_{-\infty}^{+\infty} x e^{-\beta x^2}dx$$

n is odd. So, total integration is zero.

$$\int_{-\infty}^{+\infty} x^2 e^{-\beta x^2}dx = 0 \qquad if\ n = odd$$

$$\int_{-\infty}^{+\infty} x^2 e^{-\beta x^2}dx \neq 0 \qquad if\ n = even$$

56. Correct answer is (d)

According to the pauli exclusion principle the wavefunction of fermions (here electrons) must be antisymmetric (i.e., $\psi(1,2) = -\ \psi\ (2,1)$).

For a triplet state, spin wavefunctions can be a $\alpha(1)\alpha(2)$ or $\beta(1)\ \beta\ (2)$ or $[\alpha\ (1)\ \beta\ (2) + \beta\ (1)\alpha(2)]$,which are symmetric in nature. As $\psi_{total} = \psi_{spin} + \psi_{space}$ So, for ψ_{total} to be antisymmetrical w.r.t. electron exchange, ψ_{space} , the spatial part of wavefunction is symmetrical so the spin part will be antisymmetric $\frac{1}{\sqrt{2}}[\alpha\ (1)\ \beta\ (2) -\ \beta\ (1)\alpha(2)]$

57. CORRECT OPTION (B)

Length =L

Δx=L

$\Delta p(\min) = \langle p^2\rangle^{1/2}$

$\Delta x.\Delta p_x = \frac{h}{4\pi}$

⇨ $L.\Delta p_x = \frac{h}{4\pi} => \Delta p_x = \frac{h}{4\pi L}$

$$E = \frac{p_x^2}{2m} = \frac{\left(\frac{h}{4\pi L}\right)^2}{2m} = \frac{h^2}{16\pi^2 L^2 2m} = \frac{h^2}{32\pi^2 L^2 2m} = \frac{\hbar^2}{8mL^2}$$

58. CORRECT OPTION (B)

The angukar momentum operator, $\widehat{L_z} = -i\hbar\frac{\partial}{\partial x}$ has eigen function of the form exp[imφ], where 'm' is the magnetic quantum number.

Comparing this with the eigen function given in the question ,we get

A=m

The value of m will be from –l to +l.

Since, l will be a positive integer i.e., 0,1,2,3,…

Therefore, $m = 0, \pm 1, \pm 2, \ldots$

59. CORRECT OPTION (D)

$$\int_0^L \sqrt{\frac{2}{L}}\sin\frac{n\pi x}{L}\ \delta\left(x-\frac{L}{2}\right)\sqrt{\frac{2}{L}}\sin\frac{n\pi x}{L}\ dx$$

$Dirac\ delta\ condition: \delta\left(x-\frac{L}{2}\right)=0; x=\frac{L}{2}$

The value of x→L/2 between 0→L

So, direct put the value of x=L/2 in the wave function and n=1, no integration.

$$\sqrt{\frac{2}{L}}\sin\frac{\pi L}{2L}\ \sqrt{\frac{2}{L}}\sin\frac{\pi L}{2L}=\frac{2}{L}\sin\frac{\pi}{2}\sin\frac{\pi}{2}\ =\frac{2}{L}\,.$$

60. CORRECT OPTION (A)

$S_+ = S_x + iS_y\ ; S_- = S_x - iS_y$

$[S_z, S_+] = [S_z, S_x + iS_y] = [S_z, S_x] + i[S_z, S_y]$

$= i\hbar S_y + i(-i\hbar S_x) = i\hbar S_y - i^2 S_x\hbar = i\hbar S_y + \hbar S_x = \hbar[iS_y + S_x] = \hbar S_+$

61. CORRECT OPTION (B)

Since for transition probability we habve, $T = e^{-2\beta L}$

$T = e^{\frac{2\sqrt{2m(V_0-E)}}{\hbar}L}\qquad , where\ \beta = \frac{\sqrt{2m(V_0-E)}}{\hbar}$

Transmission probability is maximum if L=minimum and V= minimum.

62. CORRECT OPTION (C)

Ground state wave function : $N_0 e^{-\sigma}$

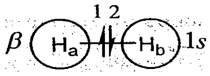
First excited state wave function :$N_1(2-\sigma)e^{-\frac{\sigma}{2}}$

The variational wave function $N_2(3-\sigma)e^{-\sigma}$ will be good approximation for the first excited state wave function. Since, the energy calculated from the varistional wave function will be greater than or equal to that of exact energy.

Therefore, $\overline{\mathrm{E}} \gg \mathrm{E}_1$.

63. CORRECT OPTION (A)

Ionic part of the ground state valence bond wave function of H_2 molecule if

$1s_a\alpha 1s_a\beta$ 

$1s_b\alpha 1s_b\beta$

Atomic spin of Hydrogen atom a and b

Ionic part : $1s_a\alpha(1)1s_a\beta(2) - 1s_a\alpha(2)1s_a\beta(1)$

$$\begin{vmatrix} 1s_a\alpha(1) & 1s_a\beta(1) \\ 1s_a\alpha(2) & 1s_a\beta(2) \end{vmatrix}$$

Covalent part: $1s_a\alpha(1)1s_b\beta(2) - 1s_a\alpha(2)1s_b\beta(1)$

$$\begin{vmatrix} 1s_a\alpha(1) & 1s_b\beta(1) \\ 1s_a\alpha(2) & 1s_b\beta(2) \end{vmatrix}$$

64. CORRECT OPTION (C)

$H\Psi_n = E_n\Psi_n$

$H\Psi_n = (E_n + V_0)\Psi_n$

In presence of extra potential function will remain same but correction term will be introduced into it in accordance with the perturbation theory.

65. CORRECT OPTION (B)

HCl is a ionic compound in valency bond theory.

HCl→ H^+(1s) +Cl^-(3p_z)

$\Psi = \Psi_H(1s.1)\Psi_{Cl}(3p_Z.2) + \Psi_{Cl}\,(3p_z.1)\Psi_H(1s.2)$

66. CORRECT OTPION (C)

In quantum mechanics, a Slater determinant is an expression that describes the wave function of a multifermionic system that satisfies anti symmetry requirements and consequently, the Pauli's principle by changing sign upon exchange of two electrons. Slater determinant is a means of ensuring the ant symmetry of a wave function through the use of matrices. A Slater determinant always corresponds to a particular spin state is not true.

67. CORRECT OPTION (B)

Energy in 1-D box=$\frac{n^2h^2}{8ml^2}$

$E_2\ (first\ excited\ sttae\ energy\ ; n = 2) = \frac{4h^2}{8ml^2}$

$E_1(ground\ state\ energy\ ; n = 1) = \frac{h^2}{8ml^2}$

$\Delta E = E_2 - E_1 = \frac{3h^2}{8ml^2}$

Energy in 2-Dbox ,$\frac{(n_x^2+n_y^2)h^2}{8ml^2}$

$E_2\big(1st\ excited\ state; (2,1)(1,2)\big) = \frac{5h^2}{8ml^2}$

$E_1(ground\ state; (1,1)) = \frac{2h^2}{8ml^2}$

Difference,$\Delta E = E_2 - E_1 = \frac{3h^2}{8ml^2}$

3-D box energy = $\frac{(n_x^2+n_y^2+n_z^2)h^2}{8ml^2}$

$E_2 = \left(first\ excited\ energy\,;(2,1,1)(1,2,1)(1,1,2)\right) = \frac{(4+1+1)h^2}{8ml^2} = \frac{6h^2}{8ml^2}$

$E_1 = \left(ground\ state\ enrgy;(1,1,1)\right) = \frac{3h^2}{8ml^2}$

$\Delta E = E_2 - E_1 = \frac{3h^2}{8ml^2}$

68. CORRECT OPTION(C)

One dimensional simple harmonic oscillator

$$\Psi_{0(x)} = \left(\frac{\beta}{\pi}\right)^{\frac{1}{4}} e^{-\frac{\beta x^2}{2}}$$

$$< x > = \int_{-\infty}^{+\infty} \Psi^* x \Psi dx \ = \int_{-\infty}^{+\infty} \left(\frac{\beta}{\pi}\right)^{\frac{1}{4}} e^{-\beta x^2/2}\, x \left(\frac{\beta}{\pi}\right)^{\frac{1}{4}} e^{-\beta x^2/2} dx$$

$$= \left(\frac{\beta}{\pi}\right)^{\frac{1}{2}} \int_{-\infty}^{+\infty} x\, e^{-\beta x^2} dx$$

In the above equation , n=1 (if n=odd, integral value =0)

Therefore , the value =0

$$< p_x > = \int_{-\infty}^{+\infty} \Psi^* p_x\, \Psi dx \ = \int_{-\infty}^{+\infty} \left(\frac{\beta}{\pi}\right)^{\frac{1}{4}} e^{-\beta x^2/2} \left(-i\hbar\frac{\partial}{\partial x}\right) \left(\frac{\beta}{\pi}\right)^{\frac{1}{4}} e^{-\beta x^2/2} dx$$

$$= \left(\frac{\beta}{\pi}\right)^{\frac{1}{2}} (-i\hbar) \int_{-\infty}^{+\infty} e^{-\beta x^2/2} \frac{\partial}{\partial x} e^{-\beta x^2/2} dx$$

$$= \left(\frac{\beta}{\pi}\right)^{\frac{1}{2}} (-i\hbar) \int_{-\infty}^{+\infty} e^{-\beta x^2/2} \left(-\frac{2\beta x}{2}\right) e^{-\beta x^2/2} dx$$

$$= (-\beta) \left(\frac{\beta}{\pi}\right)^{\frac{1}{2}} (-i\hbar) \int_{-\infty}^{+\infty} x\, e^{-\beta x^2} dx \ \ => \int_{-\infty}^{+\infty} x\, e^{-\beta x^2} dx \ = 0, if\ n = odd$$

$$= (-\beta) \left(\frac{\beta}{\pi}\right)^{\frac{1}{2}} (-i\hbar) * 0 = 0$$

$hence, < p_X > = 0.$

69. CORRECT OPTION (D)

$[x,[x,p_x]] = ?$ …(1)

$[x,p_x]\Psi = xp_x\Psi - p_x x\Psi = x\left(-i\hbar\frac{\partial}{\partial x}\right)\Psi - \left(-i\hbar\frac{\partial}{\partial x}\right)x\Psi$

$= -i\hbar x\frac{\partial\Psi}{\partial x} + i\hbar\left[\frac{x\partial\Psi}{\partial x} + \Psi\right] = -xi\hbar\frac{\partial\Psi}{\partial x} + i\hbar x\frac{\partial\Psi}{\partial x} + i\hbar\Psi = i\hbar$

From eq.(1)

$[x,i\hbar]\Psi = xi\hbar\Psi - i\hbar x\Psi = xi\hbar\Psi - xi\hbar\Psi = 0.$

70. Correct option (c)

If n = 0 , then function becomes unacceptable .

71. CORRECT OPTION (D)

$$(\hat{A}+\hat{B})(\hat{A}-\hat{B}) = \hat{A}(\hat{A}-\hat{B}) + \hat{B}(\hat{A}-\hat{B})$$
$$= \hat{A}^2 - \hat{A}\hat{B} + \hat{B}\hat{A} - \hat{B}^2$$
$$= \hat{A}^2 - \hat{B}^2 only\ if\ \hat{A}\hat{B} = \hat{B}\hat{A}$$

72. CORRECT OPTION (A)

Given, energy =3*E$_0$=3 $* \frac{3h^2}{8ml^2} = \frac{9h^2}{8ml^2}$

Therefore, degeneracy =3. (300,030,003)

73. CORRECT OPTION (A)

$\Psi = c_1 2s + c_2 \Psi 2p_z$ is normalized.

$so, c_1^2 + c_2^2 = 1\ and\ |c_1|^2 = \frac{1}{2}; |c_2|^2 = \frac{1}{2}$

$$c_1 = \pm\frac{1}{\sqrt{2}}, c_2 = \pm\frac{1}{\sqrt{2}}$$

74. CORRECT OPTION (C)

The second order correction to nth state

$$E_n^{(2)} = \frac{\sum_{m\neq n} |< \Psi_m|v|\Psi_n >|^2}{E_n - E_m}$$
$$\therefore E_1^{(2)} = \frac{|< \Psi_2|v|\Psi_1 >|^2}{E_1 - E_2}$$

75. CORRECT OTPION (B)

In radial part of wave function highest power of r denotes the value of l.

Here, l=1, and radial node=1 ⇒ 3p.

76. CORRECT OPTION (B)

$\varphi = c_1\Psi_0 + c_2\Psi_1$

$therefore, c_1^2 + c_2^2 = 1\ and \frac{c_1^2}{2} + \frac{3c_2^2}{2} = \frac{7}{6}$

$\Rightarrow (c_1^2 + c_2^2 = 1) * \frac{3}{2}$

$\Rightarrow \frac{c_1^2}{2} + \frac{3c_2^2}{2} = \frac{7}{6}$ …(1)

$\Rightarrow \frac{3c_1^2}{2} + \frac{3c_2^2}{2} = \frac{3}{2}$ …(2)

On solving equation (1) and (2), we get,

$c_1^2 = \frac{1}{3}$.

77. CORRECT OPTION (d)

If $\hat{A}$ and $\hat{B}$ commute ie,$\left[\hat{A},\hat{B}\right] = 0$, then they have same set of eigen functions.

Here, $\hat{T} = \frac{p^2}{2m} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}$; $\hat{V} = \frac{1}{2}kx^2$

$H = \hat{T} + \hat{V}$

So, $\left[\hat{H},\hat{T}\right] \neq 0 \ \ and \ \ [\hat{H},\hat{V}] \neq 0$

$\left[\hat{T},\hat{V}\right] \neq 0$.

78. CORRECT OPTION (A)

$$E = \frac{h^2}{8m}\left(\frac{n_x^2}{l_x^2} + \frac{n_y^2}{l_y^2}\right) = \frac{h^2}{8m}\left[\frac{n_x^2}{4a^2} + \frac{n_y^2}{a^2}\right] = \frac{h^2}{8m}\left[\frac{n_x^2 + 4n_y^2}{4a^2}\right]$$

$now, for\ first\ excited\ state, n_x = 2, n_y = 1$.

So, $E = \frac{h^2}{8m}\left[\frac{4+4}{4a^2}\right] = \frac{h^2}{8m}\left(\frac{2}{a^2}\right)$

Also, for the first excited state, $n_x = 1, n_y = 2$.

$$E = \frac{h^2}{8m}\left[\frac{n_x^2 + 4n_y^2}{4a^2}\right] = \frac{h^2}{8m}\left[\frac{16+1}{8m}\right] = \frac{h^2}{8m}\frac{17}{4a^2} = \frac{h^2}{8m}\left(\frac{4.25}{a^2}\right)$$

$so, minimum\ energy = \frac{h^2}{8m}\left(\frac{2}{a^2}\right) \quad ; g = 1$.

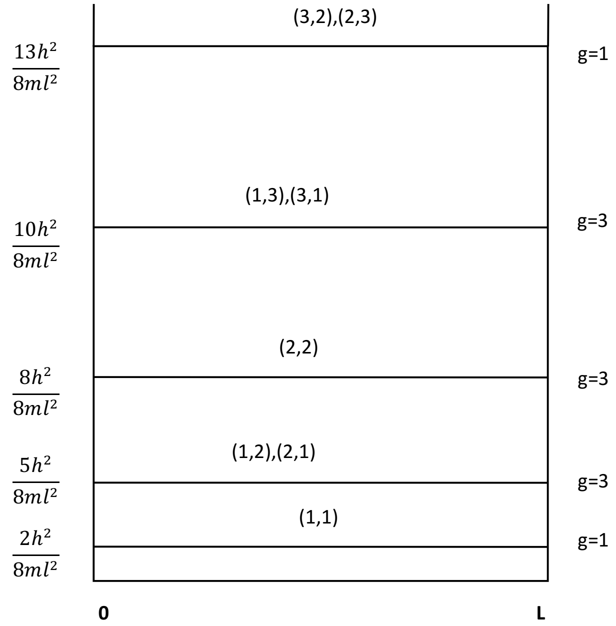


Fig: Degeneracy in 2-D box.

79. CORRECT OPTION (d)

80. CORRECT OPTION (D)

For any bound state, particle has equal and opposite value of momentum.

81. CORRECT OPTION (D)

$A|\Psi_1 \geq A|\Psi_1 > \quad and \quad H|\Psi_2 \geq b|\Psi_2 > \; ; < \Psi_2|H = B < \Psi_2|$

$a = eigen\ value.$

$< \Psi_1|A = A|\Psi_1 >^{\dagger} = a\big|\Psi_1 >^{\dagger} = a * < \Psi_1\big|$ (since, a=REAL)

$Now, < \Psi_1|[A,H]|\Psi_1 > = < \Psi_1|AH - HA|\Psi_1 > = < \Psi_1|AH|\Psi_1 > - < \Psi_1|H|a\Psi_1 >$

$= a[< \Psi_1|H|\Psi_1 > - < \Psi_1|H|\Psi_1 >] = 0$

Similarly,

$< \Psi_2|[A,H]|\Psi_2 > = < \Psi_2|AH|\Psi_2 > - < \Psi_2|HA|\Psi_2 > = b < \Psi_2|A|\Psi_2 > -b < \Psi_2|H|\Psi_2 > = 0$

82. CORRECT OPTION (C)

2s and $2p_z$ orbitals are eigen functions of L^2 & L_Z

$L_Z\, 2s = L_Z\, \psi_{200} = 0\psi_{200}$

$L_Z\, 2p_z = L_Z\, \psi_{210} = 0\psi_{210}$

$L^2 2s = L^2\psi_{200} = 0\psi_{200}$

$L^2 2p_z = L^2\, \psi_{210} = 2h^2\psi_{210}$

$L^2 2p_x = L^2 R_{21}\sqrt{\frac{3}{4\pi}}\, \sin\theta \cos\phi$

$L^2 2p_y = L^2 R_{21}\sqrt{\frac{3}{4\pi}}\, \sin\theta \sin\phi$

$L^2 2p_y = L_z R_{21}\sqrt{\frac{3}{4\pi}}\, \sin\theta \cos\phi$ Not eigen function.

Since , $L_z \rightarrow \frac{\partial}{\partial\emptyset}$ will change $\cos\phi$ to $\sin\phi$

$L^2 2p_y = L_z R_{21}\sqrt{\frac{3}{4\pi}}\, \sin\theta \sin\phi$

Therefore , not eigen functions .

$= 2h^2 R_{21}\sqrt{\frac{3}{4\pi}}\, \sin\theta \cos\phi$

$= 2h^2 R_{21}\sqrt{\frac{3}{4\pi}}\, \sin\theta \sin\phi$

83. CORRECT OPTION (D)

I.E $(He)^+ = 13.6\,\frac{z^2}{n^2} = 13.6 \times 4$

K.E +P.E = -54.4 eV …….(i)

From virial theorem,

$2\langle T\rangle = -\langle V\rangle$

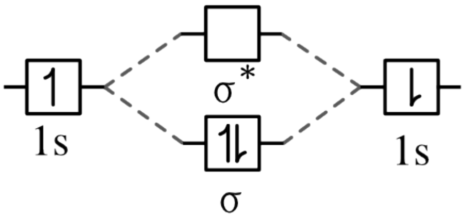
$2\langle Kinetic\ energy\ \rangle = -\langle potential\ energy\rangle$

Also, K.E = $-\frac{1}{2}\ P.E$

Therefore , from (i), $-\frac{1}{2}P.E.+P.E = -54.4$

$\frac{P.E}{2}$ = -54.4 and P.E = -108.8 eV

84. CORRECT OPTION (C)



85. Correct option (c)

For normalized wave function , $c_1^2 + c_2^2 + c_3^2 = 1$

$$\frac{1}{3}+\frac{1}{2}+\frac{1}{6}=1$$

86. Correct option (c)

E= $-13.6\frac{Z^2}{n^2} = -13.6\ \frac{5^2}{n^2} = -13.6 \Rightarrow n = 5$

orbital degeneracy= $n^2 = 25$

87 Correct option (c)

$\psi = \hat{A}\phi$ is normalized

$\int (\hat{A}\phi)^{\dagger}(\hat{A}\phi)d\tau = 1$

$\int\ \hat{A}^{\dagger}\ \phi^{\dagger}(\hat{A}\phi)d\tau = 1 \Rightarrow \int\ \phi^{\dagger}\phi d\tau = 1$

Therefore ϕ *will be normalised if* $\hat{A}^{\dagger}A = 1$

⇒ A is unitary

88 . Correct option (b)

According to perturbation theory ‘the energy of perturbed system is equal or greater than the standard system

89. Correct option (b)

$[1\sigma_g(1)\ \sigma_u(2) - 1\sigma_g(2)\sigma_u(1)]$.

$$(\psi_{1s(H_a)}(1)+\psi_{1s(H_b)}(1))\,(\psi_{1s(H_a)}(2)-\ \psi_{1s(H_b)}(2))$$
$$\left[(\psi_{1s(H_a)}(2)+\psi_{1s(H_b)}(2))\ \right]\left[(\psi_{1s(H_a)}(1)-\psi_{1s(H_b)}(1))\right]$$
$$2\left[(\psi_{1s(H_a)}(2)-\psi_{1s(H_b)}(1)-(\psi_{1s(H_a)}(1)-\psi_{1s(H_b)}(2)\right]$$

90. CORRECT OPTION (a)

The probability of finding the particle lies between x to x+dx is given by

$p(x)dx=\left(\Psi(x)\right)^2dx$

X=4,dx=δ.

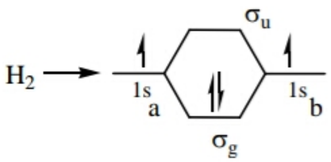
$$P_r=|\Psi|^2dx=\int\left(\sqrt{\frac{2}{L}}\sin\frac{n\pi x}{L}\ \sqrt{\frac{2}{L}}\sin\frac{n\pi x}{L}\right)dx$$
$$=\frac{2}{l}\sin^2\left(\frac{n\pi x}{l}\right)=\frac{2}{8}\sin^2\left(\frac{1*\pi*4}{8}\right)*\delta$$
$$=\frac{1}{4}\sin^2\left(\frac{\pi}{2}\right)\delta=\frac{\delta}{4}\ .$$

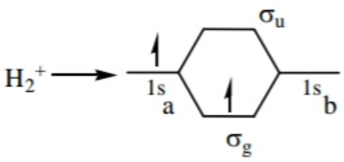
91. CORRECT OPTION (C)

$\frac{d}{dx}e^{ix}=e^{ix}$, therefore , eigen function

$\boldsymbol{\frac{d^2}{dx^2}e^{ix}=i^2e^{ix}}$, therefore, eigen function.

92. Correct option (b)





${}_2He=1s^2$; $He^+=1s^1$

H_2^+ : r → $\infty=\boldsymbol{1s_a(r)\ +\ 1sb\ (r)}$

He^+ : r → $\boldsymbol{0}=1s_{\text{He}}(r)$

93.CORRECT OPTION (C)

From the radial part $\boldsymbol{\left(6r-r^2\right)e^{-\frac{r}{3}}}$

Minimum power of $\boldsymbol{r^l=1}$

So, $\boldsymbol{l=1}$.

Corresponding to l=1, possible angular part of eigen state is cosθ

For cosθ, l=1.

94.CORRECT OPTION (B)

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{21} - ES_{21} & H_{22} - ES_{22} \end{vmatrix} = 0$$

⇨ $\begin{vmatrix} 0 - E & 2.5 \\ 2.5 & 12 - E \end{vmatrix} = 0$

⇨ -E(12-E)-6.25=0

⇨ -12E+E^2-6.25=0

⇨ E^2-12E-6.25=0

The root of this equation is E=-0.50

Therefore,E=-0.50

95. CORRECT OPTION(D)

Orbital degeneracy =n^2=6^2=36

96. CORRECT OPTION(B)

$[\hat{A}, \hat{B}\hat{C}] = [\hat{A}, \hat{B}]\hat{C} + \hat{B}[\hat{A}, \hat{C}] = 0$ { $since, [\hat{A}, \hat{B}] = 0 \; and \; [\hat{A}, \hat{C}] = 0$ }

97. CORRECT OPTION (b)let $\hat{A} = p_x$ which is hermitian perator and $\Psi = e^{-ikx}$ be operand .

$\hat{A}\Psi = \hat{A}e^{-ikx} = -\hbar k \; \Psi$

$\hat{A}^2\Psi = -\hbar^2 \frac{\partial^2}{\partial x^2}(e^{-ikx}) = +\hbar^2 k^2 e^{-ikx}$

Therefore , the eigen value is positive.

98. CORRECT OPTION (D)

Eigen functions are even values of vibratinal quantum number (n) and odd for odd values of n.

99. CORRECT OPTION (C)

In 1-D box , $\Delta E = 5 \left(\frac{h^2}{8ml^2}\right)$ and in 2-D box $\Delta E = 3 \left(\frac{h^2}{8ml^2}\right)$

And in 3-D box, $\Delta E = 3 \left(\frac{h^2}{8ml^2}\right)$

100. CORRECT OPTION (c)

For odd power of perturbed potential , $\Delta E^{(1)}$ is always 0.

101. Correct option (c)

$\pi_3 = \alpha - \sqrt{2\beta}$

$\pi_2 = \alpha$

$\pi_1 = \alpha + \sqrt{2\beta}$

$E\pi_1 \rightarrow \pi_2 = 2\ E\pi_1 \rightarrow \pi_2 \times \mathbf{4.8 = 9.6}eV$

102.Correct option (b)

$Y_{2,0} = (3cos^2\theta - 1)$, $Y_{1,0} = cos\theta$

$P_{1,2} = \int_0^{\pi} Y_{2,0}^{*} Y_{1,0}\ cos\theta sin\theta d\theta = \int_0^{\pi} (3cos^2\theta - 1) cos\theta cos\theta sin\theta d\theta$

$P_{1,2} = \int_0^{\pi} cos^2\theta (3cos^2\theta - 1) sin\theta d\theta$

103. Correct option (b)

For normalized molecular orbital must follow the total probability condition

$\psi_{sp^2} = \left(\frac{1}{\sqrt{3}}\right)\phi_{2s} + \sqrt{\frac{2}{3}}\phi_{2px}$

$\psi_{sp^2} = c_1\phi_{2s} + c_2\phi_{2px}$

$c_1^2 + c_1^2 = 1$

$c_1^2 + c_1^2 = 1$, $L.H.S.$

$c_1^2 + c_1^2 = \left(\frac{1}{\sqrt{3}}\right)^2 + \left(\sqrt{\frac{2}{3}}\right)^2 = \frac{1}{3} + \frac{2}{3} = 1$, R.H.S

If we assume ψ_1 **to** point towards x- axis , then the contribution of p_y orbital in this will be zero i.e. $C_1 = 0$

Normalization condition of ψ_1 give $a_1^2 + b_1^2 = 1$

$b_1 = \sqrt{\frac{2}{3}}$, $a_1 = \frac{1}{\sqrt{3}}$

$\psi_{sp^2} = \psi_1 = \frac{1}{\sqrt{3}}\phi_x + \sqrt{\frac{2}{3}}\phi_{2px}$

Let , three sp^2 $orbital$ are

$\psi_1 = a_1\phi_s + b_1\phi_{2px} + c_1\phi_{2py}$

$\psi_2 = a_2\phi_s + b_2\phi_{2px} + c_2\phi_{2py}$

$\psi_3 = a_3\phi_s + b_3\phi_{2px} + c_3\phi_{2py}$

For $a_1^2 + a_2^2 + a_3^2 = 1$

since the charge density of s orbital is equally divided among the three hybrid orbitals

$\Rightarrow 3\ a_1^2 = 1 \Rightarrow a_1 = \frac{1}{\sqrt{3}} \Rightarrow a_1 = a_2 = a_3 = \frac{1}{\sqrt{3}}$

In sp^2 hybridisation % of s – character is 33.3%

104. Correct option (d)

Total wave function is antisymmetric = fermions

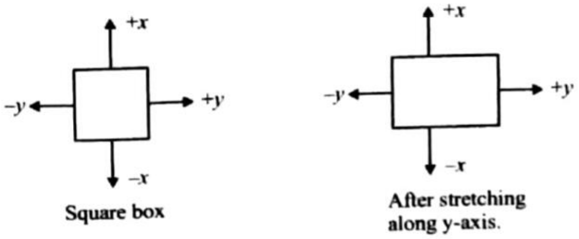
$\psi_{total} = \psi_{spin}\psi_{space}$ = [1s(1)2s(2)+2s(1)1s(2)] {spatial part }

= [1s(1)2s(2)- 2s(1)1s(2)]

α (1) α (2) ; β(1) β (2) spin part

$\frac{1}{\sqrt{2}}\alpha$ (1) β (2)+ β (l) α (2) $\Rightarrow$ $\frac{1}{\sqrt{2}}\alpha$ (1) β (2) - β (l) α (2) {spin part }

105. Correct option (d)



Square box

After stretching along y-axis.

Principle axis → z-axis

Point group symmetry	Point group symmetry
C_4 = along principle axis	C_4 = along principle axis
4 C_2 = percendicular to principle axis	2 C_2 = percendicular to principle axis
$\boldsymbol{\sigma_h}$ = along molecular plane	$\boldsymbol{\sigma_h}$ = along molecular plane
$\boldsymbol{C_4 \perp 4C_2 = D_{4h}}$	$\boldsymbol{C_2 \perp 2C_2 = D_{2h}}$

In rectangle $L_y > L_x$

Energy of particle in rectangle box is given as

$$E_{XY} = \frac{h^2}{8m^2}\left[\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2}\right]$$

$$E_{12} = \frac{h^2}{8m^2}\left[\frac{1}{L_x^2} + \frac{4}{L_y^2}\right] = \frac{h^2}{8m^2}\left[\frac{L_y^2+4L_x^2}{L_x^2.L_y^2}\right]$$

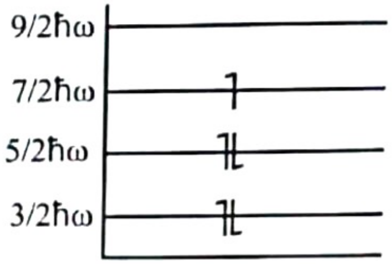
$$E_{21} = \frac{h^2}{8m^2}\left[\frac{4}{L_x^2} + \frac{1}{L_y^2}\right] = \frac{h^2}{8m^2}\left[\frac{4L_y^2+L_x^2}{L_x^2.L_y^2}\right]$$

$L_Y > L_Y$

$E_{21} > E_{12}$

106. Correct option (a)

$$E = \left(n_x + n_y + n_z + \frac{3}{2}\right)\hbar\omega$$



$$E = 2\times\frac{3}{2}\,\mathrm{h}\omega + 2\times\frac{5}{2}\,\mathrm{h}\omega + 1\times\frac{7}{2}\,\mathrm{h}\omega = \frac{21}{2}\,\mathrm{h}\omega$$

107. CORRECT OPTION (A)

$$\phi = \psi_1 + 3\psi_2$$

$H\psi_1 = E_1\psi_1$

$H\psi_2 = E_2\psi_2$

For average energy ,

$$\langle E\rangle = \frac{\langle\phi^*|\hat{H}|\phi\rangle}{\langle\phi^*\phi\rangle} = \frac{\langle(\psi_1+3\psi_2)\,|\hat{H}|(\psi_1+3\psi_2)\rangle}{\langle(\psi_1+3\psi_2).(\psi_1+3\psi_2)\rangle}$$

$$= \frac{\langle\psi_1|\hat{H}|\psi_1\rangle+3\langle\psi_1|\hat{H}|\psi_2\rangle+3\langle\psi_2|\hat{H}|\psi_1\rangle+9\langle\psi_2|\hat{H}|\psi_2\rangle}{\langle\psi_1\psi_2\rangle+3\langle\psi_1\psi_2\rangle+3\langle\psi_2\psi_1\rangle+9\langle\psi_2\psi_2\rangle}$$

$$= \frac{E_1\langle\psi_1\psi_1\rangle+3E_2\langle\psi_1\psi_2\rangle+3E_1\langle\psi_2\psi_1\rangle+9E_2\langle\psi_2\psi_2\rangle}{\langle\psi_1\psi_2\rangle+3\langle\psi_1\psi_2\rangle+3\langle\psi_2\psi_1\rangle+9\langle\psi_2\psi_2\rangle}$$

$$= \frac{E_1+9E_2}{1+9} = \frac{E_1+9E_2}{10} = \frac{E_1+9E_2}{10} \quad \begin{cases} \int \psi_i\,\psi_j = \delta_{ij} \\ \delta_{ij} = 0 \;\; if \;\; i \neq j \\ \delta_{ij} = 1 \;\; if \;\; i = j \end{cases}$$

108. CORRECT OPTION (b)

first order energy correction to the ground state is given by

$$E_0^{(1)} = \int_{-\infty}^{\infty} (\psi^0|\widehat{H^0} \quad + \widehat{H'}\,|\psi^0)dy = E_0^{(0)} + \Delta E$$

$$E_0^{(1)} \geq E_0^{(0)}$$

First order energy is not necessarily , it may be positive and zero also .

109. CORRECT OPTION (d)

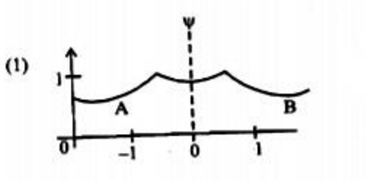
$$[\,\hat{x}\,,\hat{H}] = \left[x\,,\frac{p^2}{2m}\right] + \;[x\,,V\,(x)] \Rightarrow \frac{1}{2m}\;2p[x\,,p_x] = \frac{i\text{h}}{m}p$$

110. Correct option is (a)

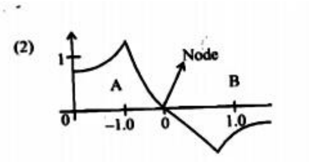
H_2^+ molecule consists of an electron orbiting about two protons (two nucleus). Here, we can assume the protons as stationary objects because the electron moves far more rapidly than protons.
The unnormalized ground-state wavefunction of the H_2^+ molecule can be formed by the linear combination of hydrogen ground state wave functions centered on each proton (nucleus).
Therefore, the unnormalized wavefunction of the H_2^+ molecule can be written as $(1)\psi_+ = \left(e^{\frac{-r_1}{a_0}} + e^{\frac{-r_2}{a_0}}\right)$ and

$$(\mathbf{2})\boldsymbol{\psi}_{-} = \left(e^{\frac{-r_1}{a_0}} - e^{\frac{-r_2}{a_0}}\right)$$

where, r_1 and r_2 are the distances between the electron and nuclei 1 and 2, respectively.



Graph of $\boldsymbol{\psi}_{+}$ w.r.t. r/a_0



Graph of $\boldsymbol{\psi}_{-}$ w.r.t. r/a_0

Since, number of nodes in $\boldsymbol{\psi}_{-}$ is greater than the number of nodes in $\boldsymbol{\psi}_{+}$, therefore $E\boldsymbol{\psi}_{-} > E\boldsymbol{\psi}_{+}$.

So, $(\mathbf{1})\boldsymbol{\psi}_{+} = \left(e^{\frac{-r_1}{a_0}} + e^{\frac{-r_2}{a_0}}\right)$will corresponds to the ground state wavefunction of H_2^+ molecule.

111. The energy eigen values of a particle of mass m in a one-dimensional box of length 2L

$$\boldsymbol{E} = \frac{\boldsymbol{n^2h^2}}{\boldsymbol{8m(2L)^2}} = \frac{\boldsymbol{n^2h^2}}{\boldsymbol{32mL^2}}$$

The energy of the level corresponding to n = 8 is

$$\boldsymbol{E} = \frac{\boldsymbol{8^2h^2}}{\boldsymbol{32mL^2}} = \frac{\boldsymbol{2h^2}}{\boldsymbol{mL^2}}$$

112 CORRECT OPTION (d)

$$P(x) = e^{-|2x-12|} = e^{-2|x-6|} = \begin{cases} e^{-2|x-6|}\ for\ x>6 \\ e^{-2|x-6|}\ for\ x>6 \end{cases}$$

113 . CORRECT OPTION (d)

Given $E(\alpha) = \frac{(\alpha^2\ -3\ \alpha)}{6}$

For variationally optimized energy, $\frac{dE}{d\alpha} = \mathbf{0} \Rightarrow \frac{1}{6}\ (\mathbf{2}\boldsymbol{\alpha} - \mathbf{3}) = \mathbf{0} \Rightarrow \boldsymbol{\alpha} = \frac{3}{2}$

For variationally optimized energy will be

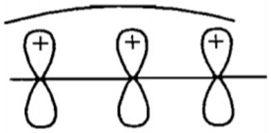
$$E\left(\boldsymbol{\alpha} = \frac{3}{2}\right) = \frac{\left(\frac{3}{2}\right)^2 - 3\left(\frac{3}{2}\right)}{6} = \frac{\frac{9}{4} - \frac{9}{2}}{6} = \frac{9-18}{4\times6} = \frac{-3}{2\times4} = \frac{3}{8}$$

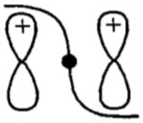
114 . CORRECT OPTION (A)

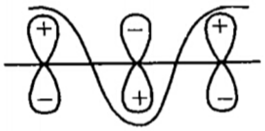
He = $1s^1\ 2s^1$

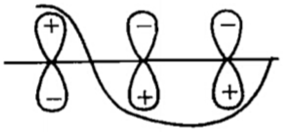
So, $\frac{1}{\sqrt{2}}\ [\alpha\ (1)\ \alpha(2) + \beta(1)\ \beta(2)]$

115 CORRECT OPTION (c).









(i) $\frac{1}{\sqrt{2}}\, x_1 + \frac{1}{2}\, x_2 + \frac{1}{\sqrt{2}}\, x_3$

$$E = \left(\frac{1}{\sqrt{2}} x_1 + \frac{1}{2} x_2 + \frac{1}{\sqrt{2}} x_3\right) \widehat{H} \left(\frac{1}{\sqrt{2}} x_1 + \frac{1}{2} x_2 + \frac{1}{\sqrt{2}} x_3\right)$$

$$= \frac{1}{2}\alpha + \frac{1}{2\sqrt{2}}\beta + \frac{1}{2\sqrt{2}}\beta + \frac{1}{4}\alpha + \frac{1}{2\sqrt{2}}\beta + \frac{1}{2\sqrt{2}}\beta + \frac{1}{2}\alpha$$

$$\frac{\left(\frac{\alpha}{1}+\frac{\alpha}{4}+\frac{\sqrt{2}\,\beta}{1}\right)}{1+\frac{1}{4}} = \left(\frac{5\alpha+4\sqrt{2}\beta}{4}\right) \times \frac{4}{5} = \alpha + \frac{4\sqrt{2}}{5}\,\beta$$

$$ii. \left(\frac{1}{\sqrt{2}}\,\chi_1 - \frac{1}{\sqrt{2}}\,\chi_3\right) \widehat{H} \left(\frac{1}{\sqrt{2}}\,\chi_1 - \frac{1}{\sqrt{2}}\,\chi_3\right) = \frac{1}{2}\alpha + \frac{1}{2}\alpha = \alpha$$

$$iii. \frac{\left(\frac{1}{2}x_1 - \frac{1}{\sqrt{2}}x_2 + \frac{1}{2}x_3\right)\widehat{H}\left(\frac{1}{2}x_1 - \frac{1}{\sqrt{2}}x_2 + \frac{1}{2}x_3\right)}{\frac{1}{4}+\frac{1}{2}+\frac{1}{4}} = \frac{\frac{1}{4}\alpha + \frac{1}{2}\alpha + \frac{1}{4}\alpha - \frac{2}{2\sqrt{2}}\beta - \frac{2}{2\sqrt{2}}\beta}{1} = \alpha - \sqrt{2}\beta$$

$$iv. \frac{\left(\frac{1}{\sqrt{2}}x_1 - \frac{1}{2}x_2 + \frac{1}{\sqrt{2}}x_3\right)\widehat{H}\left(\frac{1}{\sqrt{2}}x_1 - \frac{1}{2}x_2 + \frac{1}{\sqrt{2}}x_3\right)}{\frac{1}{2}+\frac{1}{4}+\frac{1}{2}} = \frac{\frac{1}{2}\alpha + \frac{1}{4}\alpha + \frac{1}{2}\alpha - \frac{2}{2\sqrt{2}}\beta + \frac{2}{2\sqrt{2}}\beta}{\frac{5}{4}}$$

$$= \frac{\alpha + \frac{\alpha}{4}}{\frac{5}{4}} = \frac{5\alpha}{4} \times \frac{4}{5} = \alpha$$

iii.> (ii&iv) > (i) = $\alpha - \sqrt{2}\beta > \alpha > \alpha + \frac{4\sqrt{2}}{5}\,\beta$

116. Correct option is (c)

Radial part of the wave function of hydrogen atom is proportional to $e^{-\frac{r}{na_0}}$

Comparing $e^{-\frac{r}{3a_0}}$ with $e^{-\frac{r}{na_0}}$ we get n = 3

The maximum power of cosθ is 2. So, l = 2. Minimum power of r is 2. So, l = 2

Angular part of the wave function of hydrogen atom is proportional to $e^{im\phi}$

Since, there is no ∅ dependence in the wave function. Therefore, m = 0

117 . Correct option is (c)

Radial part of the wave function of hydrogen atom is proportional to $e^{-\frac{r}{na_0}}$

Comparing $e^{-\frac{r}{3a_0}}$ with $e^{-\frac{r}{na_0}}$ we get n = 3

The maximum power of cosθ is 2. So, l = 2. Minimum power of r is 2. So, l = 2

Angular part of the wave function of hydrogen atom is proportional to $e^{im\phi}$

Since, there is no ϕ dependence in the wave function. Therefore, m = 0

Orbital = 3d

118. Correct option is (a)

Energy in 3-D cubic box having length, L = $\frac{(n_x^2+n_y^2+n_z^2)h^2}{8mL^2}$

Energy = $\frac{27h^2}{8mL^2}$

Possible arrangement

$(3^2 + 3^2 + 3^2) = 27$; $n_x = 3, n_y = 3, n_z = 3$
$(5^2 + 1^2 + 1^2) = 27$; $n_x = 5, n_y = 1, n_z = 1$
$(1^2 + 5^2 + 1^2) = 27$, ; $n_x = 1, n_y = 5, n_z = 1$
$(1^2 + 1^2 + 5^2) = 27$, ; $n_x = 1, n_y = 1, n_z = 5$

Total degeneracy=4

119. Correct option is (d)

In dominant resonance structure LiH exist as Li^+H^- , where both electrons lie to hydrogen atom.

The spatial part of the dominant resonance structure of the LiH molecule is

$\phi = 1s_H(r_1)\, 1s_H(r_2)$

120. Correct option is (2)

$$\text{(A)}\left(\frac{d^2}{dx^2} - x^2\right) e^{\frac{-x^2}{2}} = \frac{d^2}{dx^2} e^{\frac{-x^2}{2}} - x^2 e^{\frac{-x^2}{2}}$$

$$\left(\frac{d}{dx}\frac{d}{dx} e^{\frac{-x^2}{2}}\right) - x^2 e^{\frac{-x^2}{2}} = \frac{d}{dx}\left(-\frac{2x}{2} e^{\frac{-x^2}{2}}\right) - x^2 e^{\frac{-x^2}{2}}$$

$$(\frac{d}{dx} - x\, e^{\frac{-x^2}{2}}) - x^2 e^{\frac{-x^2}{2}} = -\left[\frac{d}{dx} x\, e^{\frac{-x^2}{2}}\right] - x^2 e^{\frac{-x^2}{2}}$$

$$-\left[x\left(-\frac{2x}{2}\right) e^{\frac{-x^2}{2}} + e^{\frac{-x^2}{2}}\right] - x^2 e^{\frac{-x^2}{2}}$$

$$= x^2 e^{\frac{-x^2}{2}} - e^{\frac{-x^2}{2}} - x^2 e^{\frac{-x^2}{2}}$$

$$= -e^{\frac{-x^2}{2}} = (-1)e^{\frac{-x^2}{2}}[eigen\ function]$$

$$(B)\left(\frac{d^2}{dx^2} + x^2\right) e^{\frac{-x^2}{2}} = \frac{d^2}{dx^2} e^{\frac{-x^2}{2}} + x^2 e^{\frac{-x^2}{2}} = \left(\frac{d}{dx}\frac{d}{dx} e^{\frac{-x^2}{2}}\right) + x^2 e^{\frac{-x^2}{2}}$$

$$\frac{d}{dx}\left(-x e^{\frac{-x^2}{2}}\right) + x^2 e^{\frac{-x^2}{2}}$$

$$= x^2 e^{\frac{-x^2}{2}} - e^{\frac{-x^2}{2}} + x^2 e^{\frac{-x^2}{2}} = 2x^2 e^{\frac{-x^2}{2}} - e^{\frac{-x^2}{2}} = e^{\frac{-x^2}{2}}[2x^2 - 1]$$

Not ***eigen function***, not having eigenvalues.

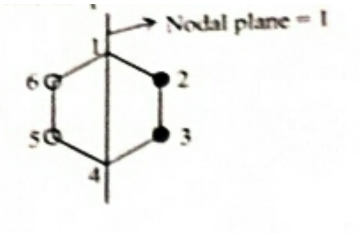
(C) $\frac{d}{dx}\frac{d}{dx}\cos\frac{\pi x}{4} = \frac{d}{dx} - \left(\frac{\pi}{4}\right)\sin\frac{\pi x}{4}$

$= -\left(\frac{\pi}{4}\right)\frac{d}{dx}\sin\frac{\pi x}{4} = -\left(\frac{\pi}{4}\right)^2 \cos\frac{\pi x}{4}$ $[\boldsymbol{eigen\ function}]$

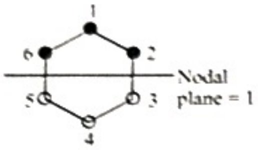
(D) $\frac{d}{dx}\frac{d}{dx}e^{4ix} = \frac{d}{dx}(\boldsymbol{4i})e^{4ix} = e^{4ix}(4i)^2 = -16\ e^{4ix}$ $[\boldsymbol{eigen\ function}]$

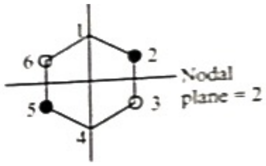
121. Correct option is (a)

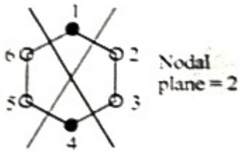
Given molecular orbital in questions:

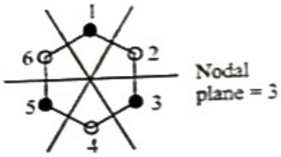


Check options:

(a)


(b)


(c)


(d)


Since, in question number of plane = 1 in option (a) has one to nodal plane. Hence, these are degenerate states.

122.Correct option is (d)

The linear variation method provides upper bounds to the energies of the lowest n bound states of the system

A linear variation function is a linear combination of n linearly independent functions.

$f_1 + f_2 + f_3 + \ldots\ldots\ldots f_n$

$\boldsymbol{\phi = c_1}f_1 + c_2f_2 + c_3f_3 + \ldots\ldots\ldots c_nf_n = \sum_{j=1}^{n} \mathbf{c_i f_i}$

The variation integral W is, $W = \frac{\int \phi^* \hat{H} \phi d\tau}{\int \phi^* \phi d\tau}$

The solution of above function has n roots. Arranging these roots in order of increasing value, we denote them as $W_1 \leq \boldsymbol{W_2} \leq \boldsymbol{W_3}$ ....$\leq \boldsymbol{W_n}$

If we number of bound states of the system in order of increasing energy, we have

$E_1 \leq \boldsymbol{E_2} \leq \boldsymbol{E_3} \ldots. \leq \boldsymbol{E_n} \leq \boldsymbol{E_{n+1}} \leq \ldots.$

where E's denote the true energies of various states. From the variation theorem, we know that $\boldsymbol{E_1} \leq W_1$

123. Correct option (a)

ψ_{n_x,n_y,n_z} (x, y, z) = $\left(\frac{2}{l}\right)^{\frac{3}{2}} \sin\frac{2\pi x}{l} \sin\frac{2\pi y}{l} \sin\frac{2\pi z}{l}$

Here , $n_{x=2}$, $n_{y=3}$, $n_{z=2}$

The energy spectrum , is

$$E_x = \frac{n_x^2h^2}{8ml^2},\ E_y = \frac{n_y^2h^2}{8ml^2},\ E_z = \frac{n_z^2h^2}{8ml^2}$$

$$\langle E\rangle = \frac{\langle P^2\rangle}{2m}\ ;\ \langle P^2\rangle = 2m\langle E\rangle$$

$$\langle P^2\rangle = 2m\langle E_x\rangle + 2m\langle E_y\rangle + \langle 2mE_z\rangle = 2\text{m}\left[\langle E_x\rangle + \langle E_y\rangle + \langle E_z\rangle\right]$$

$$2\text{m}\left[\frac{4h^2}{8ml^2} + \frac{9h^2}{8ml^2} + \frac{4h^2}{8ml^2}\right] = 2\text{m} \times \left[\frac{17h^2}{8ml^2}\right] = \frac{17h^2}{4l^2}$$

124. Correct option is (d)

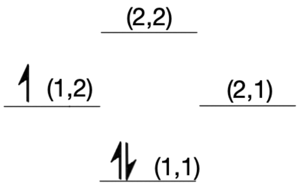
The energy spectrum for two dimensional square box of length L is,

$E_{nx,ny} = \frac{(n_x^2+n_y^2)h^2}{8ml^2}$ $\{l_x = l_y = l\}$

Three non-interacting Electron

Electron (spin 1/2), act as a fermion

2 spin half electrons filled in one energy levels



Ground state energy= $2\,\frac{(1^2+1^2)h^2}{8ml^2}$ +1 .$\frac{(2^2+1^2)h^2}{8ml^2} = \frac{4h^2}{8ml^2} + \frac{5h^2}{8ml^2} = \frac{9h^2}{8ml^2}$

125. The eigen functions are = $\phi_l(\phi) = \frac{1}{\sqrt{2\pi}} e^{im_l\phi}$

Therefore, the first order correction due to a perturbation H'=uEcos ϕ will be,

$$E_l^{(0)} = \langle\phi_l^*|H'|\phi_l\rangle = \frac{\mu E}{2\pi}\int_0^{2\pi} e^{-im_l\phi}\cos\phi . e^{im_l\phi}\, d\phi = \frac{\mu E}{2\pi}\,|\sin\pi|_0^{2\pi} = 0$$

The original energy is, $E_l = \frac{m_l^2\,\text{h}^2}{2}$.Therefore, the corrected energy (upto first order) is, $E_l + E_1^{(0)} = \frac{m_l^2\,\text{h}^2}{2I} + 0 = \frac{m_l^2\,\text{h}^2}{2I}$

Correct option is (d)

126. Correct option is (b)

For He^+

$He^+ = 1s^1$ (one electron system) [l= 0 ,n= 1, z=2]

$$\boldsymbol{\langle r\rangle = \frac{a_0}{2z}[3\times n^2 - l(l+1)] = \frac{a_0}{2\times 2}[3\times 1^2 - 0(0+1)];\ \langle r\rangle = \frac{a_0}{4}[3-0] = \frac{3a_0}{4}}$$

127. Correct option (a)

$$\mathrm{H} = \frac{p_x^2}{2m} + \mathrm{V(x)} \quad ; \quad \mathrm{P_X} = -\mathrm{i}\mathrm{h}\frac{\partial}{\partial x}$$

[H, x]

$$\mathrm{H} = \frac{1}{2m}\left(-\mathrm{i}\mathrm{h}\frac{\partial}{\partial x}\right) + \mathrm{V_X}\ ;\ \mathrm{H} = \frac{-\mathrm{h}^2}{2m}\left(\frac{\partial^2}{\partial x^2}\right) + \mathrm{V_X}$$

$$[\mathrm{H, x}]\psi_x = \left[\left(\frac{-\mathrm{h}^2}{2m}\left(\frac{\partial^2}{\partial x^2}\right) + \mathrm{V_x}\right)x\right]\psi_x = \left[\frac{-\mathrm{h}^2}{2m}\left(\frac{\partial^2}{\partial x^2}\right) + \mathrm{V_x}\right]\psi_x$$

$$= \frac{-\mathrm{h}^2\left(\frac{\partial^2}{\partial x^2}\right)x\psi_x +}{2m} + \mathrm{V_x}\,x\psi_x + x\frac{-\mathrm{h}^2}{2m}\left(\frac{\partial^2}{\partial x^2}\right)\psi_x - \mathrm{xV_x}\,\psi_x$$

$$= \frac{-\mathrm{h}^2}{2m}\frac{\partial}{\partial x}\frac{\partial}{\partial x}(x\psi_x) + x\frac{-\mathrm{h}^2}{2m}\left(\frac{\partial^2}{\partial x^2}\right)\psi_x = \frac{-\mathrm{h}^2}{2m}\frac{\partial}{\partial x}\left[x\frac{\partial}{\partial x}\psi_x + \psi_x\right] + x\frac{\mathrm{h}^2}{2m}\left(\frac{\partial^2}{\partial x^2}\right)$$

$$= \frac{-\mathrm{h}^2}{2m}\frac{\partial}{\partial x}\left(x\frac{\partial}{\partial x}\psi_x\right) - \frac{\mathrm{h}^2}{2m}\frac{\partial}{\partial x}\psi_x + x\frac{\mathrm{h}^2}{2m}\left(\frac{\partial^2}{\partial x^2}\right)\psi_x$$

$$= \frac{-\mathrm{h}^2}{2m}\left[x\left(\frac{\partial^2}{\partial x^2}\right)\psi_x + \frac{\partial}{\partial x}\psi_x\right] - \frac{\mathrm{h}^2}{2m}\frac{\partial}{\partial x}\psi_x - \frac{\mathrm{h}^2}{2m}\frac{\partial}{\partial x}\psi_x + x\frac{\mathrm{h}^2}{2m}\left(\frac{\partial^2}{\partial x^2}\right)\psi_x$$

$$= \frac{-\mathrm{h}^2}{2m}x\left(\frac{\partial^2}{\partial x^2}\right)\psi_x - -\frac{\mathrm{h}^2}{2m}\frac{\partial}{\partial x}\psi_x - -\frac{\mathrm{h}^2}{2m}\frac{\partial}{\partial x}\psi_x + x\frac{\mathrm{h}^2}{2m}\left(\frac{\partial^2}{\partial x^2}\right)\psi_x$$

$$= \frac{-2\mathrm{h}^2}{2m}\frac{\partial}{\partial x}\psi_x = -\frac{\mathrm{h}^2}{m}\frac{\partial}{\partial x} = -\frac{\mathrm{h}}{m}(-\mathrm{h})\frac{\partial}{\partial x} = \left[\frac{\mathrm{h}}{im}\left(-\mathrm{i}\mathrm{h}\frac{\partial}{\partial x}\right)\right] = \frac{\mathrm{h}}{im}\,\mathrm{px} = \frac{-i\hbar}{m}\,\mathrm{p_x}$$

128. Correct option (b)

Since, $[\hat{x}, \hat{p}_x{}^n] = ni\hbar\hat{p}_x{}^{n-1}$

Putting $n = 2$ in the above relation, we get

$[\hat{x}, \hat{p}_x{}^2] = 2i\hbar\hat{p}_x$

129. Correct option (a)

Since, it is not mentioned in the question about the wavefunction, hence, for total molecule, the – electron density is distributed equally over all the carbons. $q_i = \sum n_i a_{ij}^2$

130. Correct option (c)

Since we know,

$E = \frac{1}{2}mv^2$

$$\therefore\ \langle E\rangle = \frac{1}{2}m\langle v^2\rangle$$

$$\Rightarrow \langle v^2\rangle = \frac{2\times\langle E\rangle}{m}$$

$$\Rightarrow \frac{2\times 13.6\times 1.6\times 10^{-19}}{9.1\ \times 10^{-31}} \approx 4.7\times 10^{12}$$

131. Correct option (b)

The perturbation given in the question (V = E.z) is electric field perturbation, which is Stark effect perturbation along z-axis. This is highly dependent on *m* values, for orbital 2s and $3d_z^2$ the *m* value = 0, thus option (a) and option (d) are incorrect. In option (c), $3p_y$ orbital is oriented towards y-axis, thus its contribution will be negligible, hence, correct answer is option (b)

13

Group Theory

Hints & Solutions

1. Correct option (a)

$$\Gamma_{A1} = \frac{1}{6}\left[(6\times1)+(2\times1\times3)+(3\times1\times0)\right]=2$$

$$\Gamma_{A2} = \frac{1}{6}\left[(6\times1)+(2\times1\times3)+(3\times-1\times0)\right]=2$$

$$\Gamma_{E} = \frac{1}{6}\left[(6\times2)+(2\times-1\times3)+(3\times0\times0)\right]=1$$

$$T = 2A_1 + 2A_2 + E$$

2. Correct option (d)

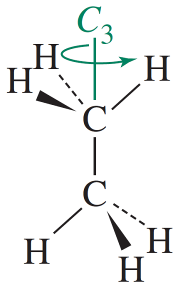
The direct product of two energy state should transform accoeding to x,y or z axis for electronic transition

$A_1 * A_1 = A_1$ = transform with z axis = allowed

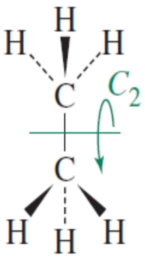
QUANTA POINT

A_1* E=E = transform with x,y axis = allowed
A_2* E= E = transform with x,y axis = allowed
A_1* A_2= A_2 = transform with x,y or z axis = FORBIDDEN

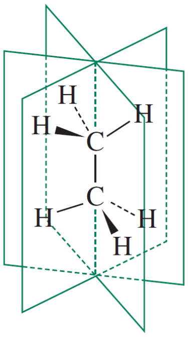
3. Correct answer (b)
Staggerd ethane- point group –D_{3d}.



H_3CCH_3



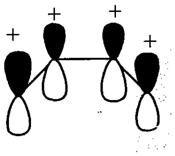
H_3CCH_3

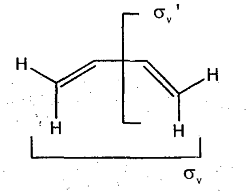


H_3CCH_3

4. Correct option (c)
Ψ_1= P_1+$2P_2$+$2P_3$+P_4 (equation shows 0 nodes)

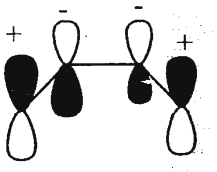
E	C_2	σ_v	σ_v'
1	-1	-1	1





This belongs toB_2.

Ψ_2= 2P1-P2-P_3+$2P_4$ (equation shows 2 nodes)



E	C_2	σ_v	σ_v'
1	-1	-1	1

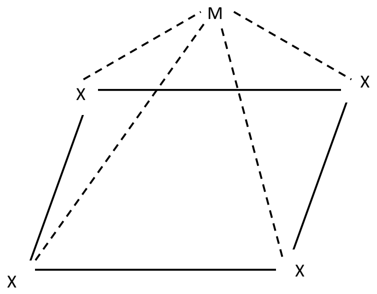
This belongs toB_2.

5. Correct option (a)
The number of irreducible representations is equal to number of classes of symmetry operations in the group. This is the first postulate of Great Orthogonality Theorem (GOT).

6. Correct option (a)

E	$2C_2$	C_2	$2\sigma_v$	$2\sigma_d$

5	1	1	1	3



7. Correct option (c)

   Transition A_1 to B_1 can be evaluated by direct product A_1 x B_1 and its transition.

   A_1 x B_1 =

E	C_2	σ_V	$\sigma_{V'}$	
1	1	1	1	
X	X	X	X	
1	-1	1	-1	
1	-1	1	-1	=B_1

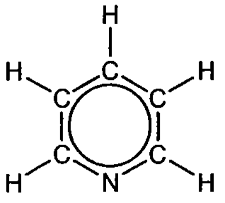
   B_1 transforms A1 to B1 according to x axis and hence, transition will be x- polarized.

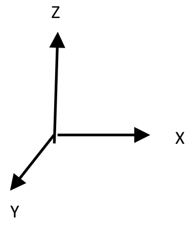
8. Correct option (d)

   B_2H_6 has D_{2h} point group and S_2 axis.
   CH_4 has Td point group and S_4 axis.
   PH_5 has D_{3h} point group and S_3 axis.
   SF_6 has O_h point group and S_6 axis.
   So, SF_6 has S_6 axis.

9. Correct option (c)

   C_5H_5N





   C_{2V} point group.

   Reducible representation by 3N coordinates.

C_{2V}	E	C_2	σ_v	$\sigma_{v'}$

R.R.	33	-3	3	11

n_{A1} = (¼)[33-3+3-11]=11. n_{A2} = (¼)[33-3-3-11]=4.

n_{B1} = (¼)[33+3+3-11]=7. n_{B2} = (¼)[33+3-3+11]=11.

R.R.= $11A_1+4A_2+7B_1+11B_2$

Rotational= $A_2+B_1+B_2$

Translational= $A_1+B_1+B_2$

Vibrational=10 A_1+ $3A_2$+ 5B1+9 B_2= 27

Out of 27 ,3A_2 are IR inactive.

So, Total IR active 10 A_1+5B1+9 B_2

Total vibrations=24 vibrations.

10. Correct option (c)

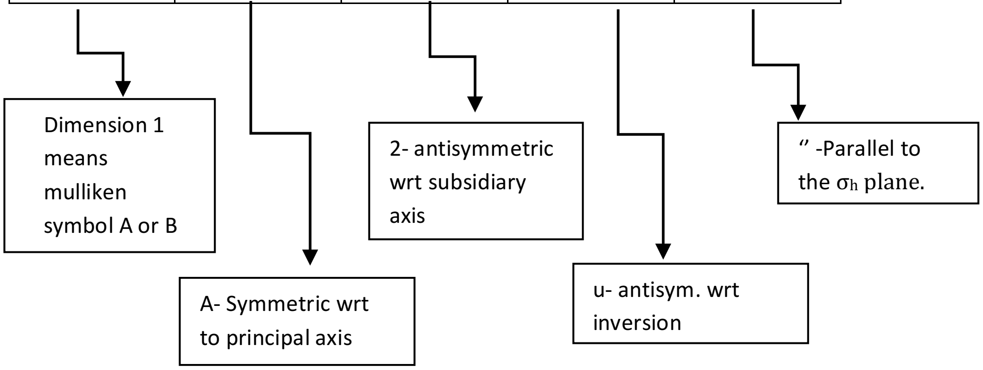
Number of classes: E, $2C_6$, $2C_3$, C_2 , $3\sigma_d$, $3\sigma_v$ => 6

Total operation=1+1+1+1+1+1=6

Order = 1+2+2+1+3+3=12

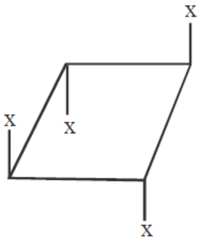
11. Correct option (b)

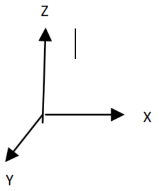
E	C_n	nC_2	i	σ_h
1	1	-1	-1	-1


Dimension 1 means mulliken symbol A or B
A- Symmetric wrt to principal axis
2- antisymmetric wrt subsidiary axis
u- antisym. wrt inversion
" -Parallel to the σ_h plane.

So, A''_{2u} will be Mulliken symbol.

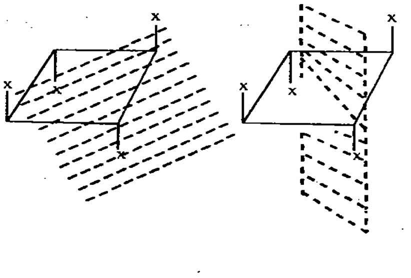
12. CORECT OPTION (C)





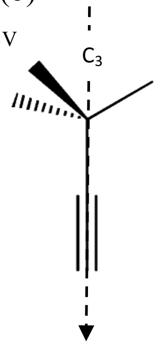
The structure has 3 C_2 axis perpendicular to each other. If C_2 (z) is P-axis. Then, there is two vertical plane also.

$C_2+2C_2+2\sigma_v= D_{2d}$ point group.



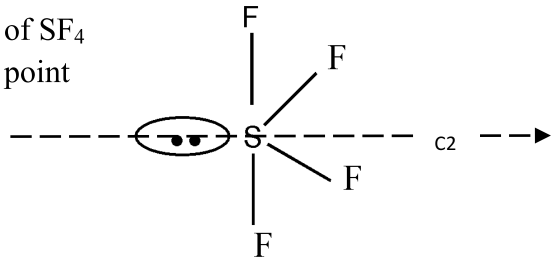
13. Correct option (b)
    If the direct product of ground and excited state transforms according to the x,y,z axis then the transition will be allowed.
    A_g x B_g= 1×1,1×-1,-1×1,-1×-1
    = 1,-1,-1,1
    = B_u.
    And B_u transforms as per x –axis . hence , B_g to A_g transition will be x- polarized.

14. Correct option (b)
    PROPYNE- C_{3V}



15. Correct answer (d)
    The triclinic crystal with parameters a≠b≠c and $\alpha\neq\beta\neq\gamma\neq90^0$ is least symmetric. Therefore, no axis of symmetry.

16. Correct option (d)
    The low temperature (–98ºC) ^{19}F NMR spectrum of SF_4 shows doublet of triplets. It is consistent with the point group symmetry C_{2V}.



17. Correct option (a)

E×E =

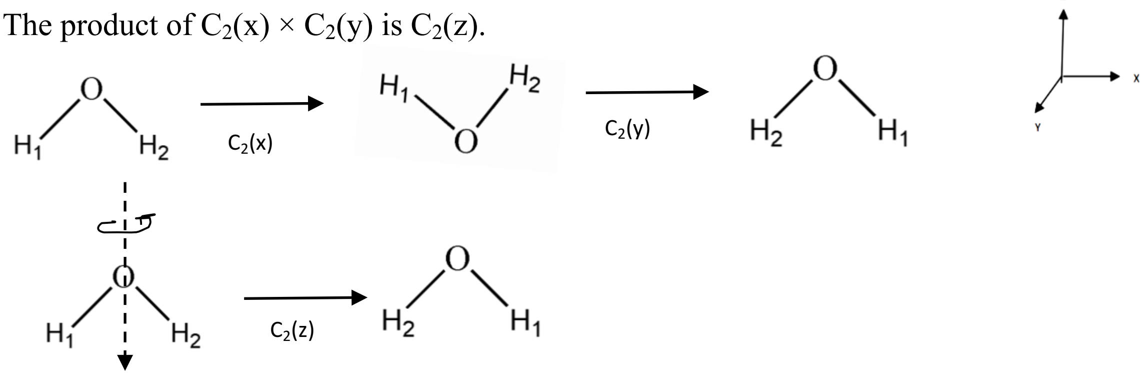
2×2	(-1)×(-1)	0×0
4	1	0

$n_{A1} = (1/6)\ [4+2+0]=1$; $n_{A2} = (1/6)[4+2-0]=1$; $n_E = (1/6)[8-2-0]=1$

Therefore, E X E= A_1+A_2+E

18. Corect option (c)

The product of $C_2(x) \times C_2(y)$ is $C_2(z)$.

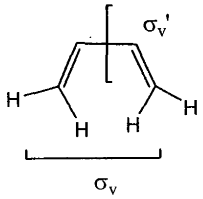


19. Option coorect(a)

Check the structures.

20. Correct option (d)

C_{2V}	E	C_2	σ_v	$\sigma_{v'}$
No. of unshifted atoms	10	0	0	10
Contribution per atom	3	-1	1	1
Reducible representation	30	0	10	0



$n_{A1} = (¼)[30+0+10+0]=10.$ $n_{A2} = (¼)[30-10]=5.$

$n_{B1} = (¼)[30+0+10+0]=5.$ $n_{B2} = (¼)[30+10]=10.$

R.R.= $10A_1+5A_2+5B_1+10B_2$

ROTATIONAL= $A_2+B_1+B_2$

TRANSLATIONAL= $A_1+B_1+B_2$

VIBRATIONAL= TOTAL- (ROT.+TRANS)

$= 10A_1+5A_2+5B_1+10B_2- [A_2+B_1+B_2+A_1+B_1+B_2]$

$=9A_1+3B_1+8B_2$

21. Correct answer (a)

$\sigma^{xy}\ x\ S_4^{z}= \sigma^{xy}\ x\ C_4^{z}\ x\ \sigma^{xy} = C_4^{z}(\sigma^{xy}\ x\ \sigma^{xy}) = C_4^{z}\ x\ E = C_4^{z}$

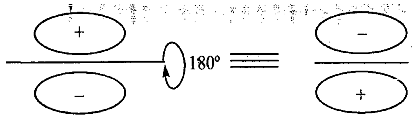
22. Correct option (a)

$(x,y,z) \xrightarrow[\sigma_{xy}]{} (x,y,-z) \xrightarrow[C_2^x]{} (x,-y,z)$

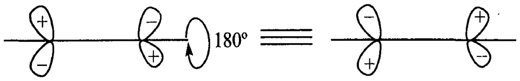
So, $C_2^x \times \sigma_{xy} = \sigma_{xz}$

23. Correct option (b)

If the sign is changed it is called ''π''.



π-BMO



π^*-ABMO

24. Correct option (d)

	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$
IRR	15	0	-1	-1	3

$n(A)=1$; $n(E)=1$; $n(T_2)=3$; $n(A_2)=0$; $n(T_1)=1$

IRR= $A_1 + E + T_1 + 3T_2$

Translational = T_2

Rotational = T_1

So, normal modes of vibration= $A_1 + E + 2T_2$

Now IR active modes= T_2.

25. Correct option- (d)

$C_2 + 2c_2 + 2\sigma_v + 1\sigma_h = D_{2h}$

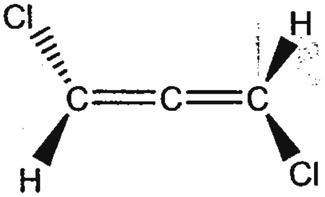
26. Correct option (a)

Raman active vibrations transform according to quadratic functions of x,y and z which are A_g and B_g.

27. Correct option (a)

The molecule is chiral.

Therefore, no plane, only one C_2.



28. Correct option (b)

$C_4 + 1\sigma_h \Rightarrow C_{4h}$.

29. Correct option (d)

From column (3) and (4) ,infront of ''E'' irreducible representations , it is clear that there is a pair of IR active modes which are degenerate.

Degeneracy of E=2.

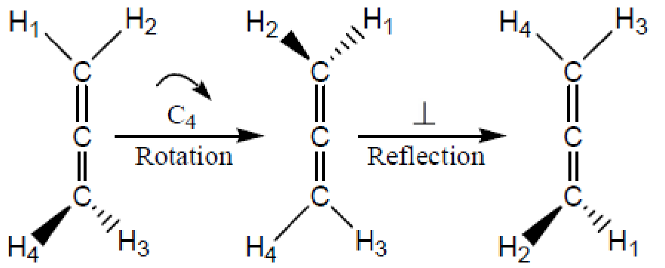
30. Correct option (b)

$\Gamma_{A1} = (1/6)\,[6\times1\times1+0+2\times3\times1]=2$

$\Gamma_{A2} = (1/6)\,[6\times1\times1+0-6]=0$

$\Gamma_{E} = (1/6)\,[6\times2+0+0]=2$

31. Correct option (b)



Equivalent

32. Correct option (b)

A_1	1	1	1	1	
B_1	1	−1	1	−1	
$A_1\times B_1 =$	1	−1	1	−1	⇒ x polarized

33. Correct option (d)

The polar point group are

$C_{nv}\ , C_n, C_1\ , C_s$

34. Correct option (d)

$S^3_6 = C_6^3 \times \sigma^3 = C_2^1 \times \sigma = S_2$.

35. Correct option (c)

Character table of C_{3v} points group and complete table is : (appyling GOT we can obtain A_2)

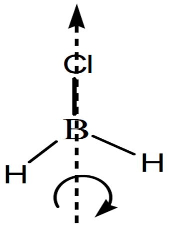
C_{3V}	E	$2C_3$	$3\sigma_V$
A_1	1	1	1
A_2	1	1	-1
E	2	-1	0

36. Correct option (d)

A_2'' :- A- symmetric wrt C_3 (principal axis), 2- antisymm. wrt C_2 and ('') for the given vibrational is not symmetric wrt σ_h.

37. Correct option(a)

Once C_2 passing through B andCl atoms, two hydrogen interchange the Position but remain same molecule.

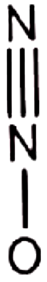


38. Correct option : (a)

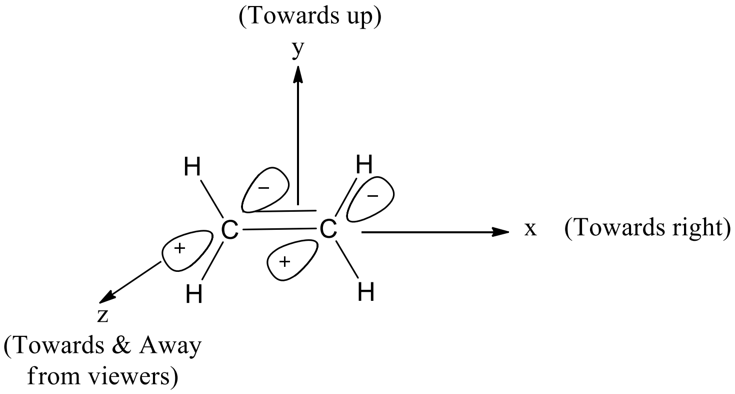
According to GOT theorem, any two IR must be orthogonal to each other.

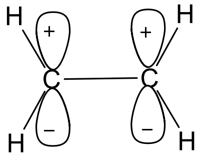
39. Correct option (b)

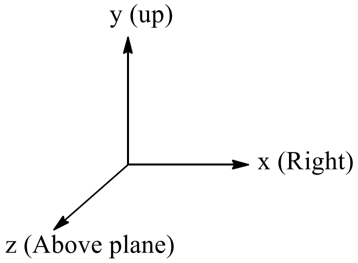
$1C_\infty + \infty C_V = C_{\infty V}$



40. If ethylene molecule is i -plane







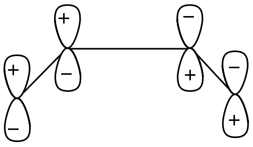
E	C2(z)	C2(y)	C2(x)	i	σxy	σxz	σyz
1	1	−1	−1	−1	−1	1	1

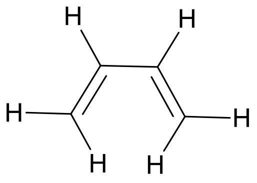
Which suggests, it should be B_{1u}

41. Correct option (d)

$$B_{1u}\times B_{2g} = 1 \quad -1 \quad -1 \quad 1 \quad -1 \quad 1 \quad 1 \quad -1 \quad \Rightarrow \quad z\ (\boldsymbol{B_{3u}})$$

42. Correct option (b)





The correct irreducible representation corresponding to the above π-orbital for cis-butadiene is

	E	C_2	σ_v	$\sigma_v{}'$
A_2	1	1	−1	−1

43. Correct option (b)

The representation Γ for the C_{2v} point group is as

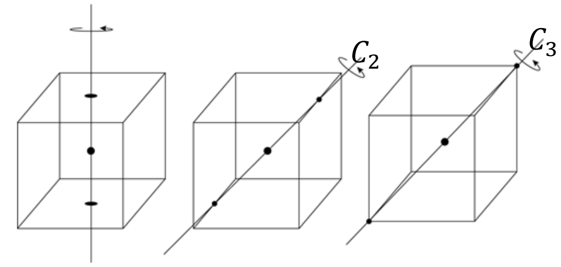
	E	C_2	σ_v	$\sigma_v{}'$
Γ	3	1	1	3

The number of irreducible $A_1 = \frac{1}{4}[3\times1\times1 + 1\times1\times1 + 1\times1\times1 + 3\times1\times1]$

$$= \frac{1}{4}[3+1+1+3] = \frac{1}{4}\times8 = 2$$

44. Correct option (d)

C_4



C_4: Passing through two opposite faces
C_2: Passing through two opposite edges
C_3: Passing through two opposite corners, containing body diagonal.

45. Correct option (b)

A_1	1	1	1	1
$2A_2$	2	2	–2	–2
$5B_2$	5	–5	–5	5
$A_1 + 2A_2 + 5B_2$	8	–2	–6	4

46. Correct option (b)

$f_1 \in A_2$ and $f_2 \in B_1$

$A_2 \times B_1 = B_2$

Since the product does not belong to totally symmetric representation (A_1) so the integral $\int f_1 f_2 d\tau$ must be zero.

47. Correct option (b)

$\Gamma_{vib} = A_1' + 2E' + A_2''$

A_1' is Raman active only. E' is both Raman and IR active (doubly degenerate), A_2'' is IR active only. IR bands 995, 480, 244 (in cm^{-1})

Since bands at 995 cm^{-1} and 244 cm^{-1} are observed in both Raman and IR spectrum, they must be $2E'$. The other Raman band observed at 471 cm^{-1}, so it will be A_1'

48. Correct option (a)

$S_3^2 = C_3^2.\sigma^2 = C_3^2.E = C_3^2.\sigma^2$

Trace of $C_3^2 = -\frac{1}{2} - \frac{1}{2} + 1 = 0$

49. Correct option (c)

Not shifting means unchanged orientation, and in such case the most logical answer would be option (c) 1,1 but it can vary depending upon the molecule.

50. Correct option is (d).

The first operation can be simplified as,
$S_6^3 = S_2 = i$.
And for S_n^{2n} where n= odd, we get, S_n^{2n}= E.

Data Analysis

Hints & Solutions

1. Correct option (d)

since , $y2 = 4x$

after 1% increase in value of x

$y = \sqrt{4x}$

$y = 2x^{1/2}$

$$\frac{\Delta y}{y}\times 100 = \frac{1}{2}\frac{\Delta x}{x}\times 100$$

% error in $y = \frac{1}{2}\times$ % error in x

$$= \frac{1}{2}\times 0.1 = 0.05$$

2. Correct option (b)

for data set $\{X_i Y_i\}$. when equation is Y=AX+B

its deviation are taken from middle period so that $\sum X = 0$, the value of A and B can be directly written

as $A = \frac{\sum XY}{\sum X^2}$ and $B = \frac{\sum Y}{N}$

QUANTA POINT

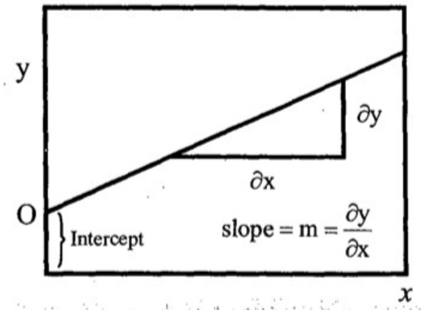
3. Correct option (b)

For A, RSD = $\frac{\text{FWW}\times\text{G}}{\text{XW}}= 4$

For B, RSD = $\frac{\text{FWW}\times\text{G}}{\text{FWW}}= 2$

More RSD less precise, less RSD more precise.

4. Correct option (c)



for value of slope m = $\frac{\delta y}{\delta x}$

$$m_{[} = \frac{\partial y}{\partial x} = \frac{y_{\text{G}} - y_{\text{F}}}{x_{\text{G}} - x_{\text{F}}} = \frac{11.3 - 11.1}{4.4 - 4.3} = \frac{0.2}{0.1} = 2$$

$$m_{\wedge} = \frac{\partial y}{\partial x} = \frac{y_{\text{G}} - y_{\text{F}}}{x_{\text{G}} - x_{\text{F}}} = \frac{11.5 - 10.9}{4.4 - 4.3} = \frac{0.6}{0.1} = 6$$

thus $m_{\wedge} > m_{[}$ and for the value of $c_{\wedge} < c_{[}$

5. Correct option (d)

if two arbitrary variables x and y then measure of intensity of correlation coefficient

$$r = \frac{n\,[\sum xy - \sum x \sum y]}{\sqrt{[n\sum x^{\text{G}} - (\sum x)^{\text{G}}][n\sum y^{\text{G}} - (\sum y)^{\text{G}}]}}$$

if $\langle xy \rangle = x\langle\ \ \rangle\langle y \rangle$

$\Rightarrow \sum xy = \sum x \sum y$

$\Rightarrow [r = 0]$

QUANTA POINT

6. Correct option (a)

the value of correlation coefficient lies between -1 to +1

the value found -0.99 near -1 mean strongly correlate if value outside of -1 to +1 almost on correlated

7. Correct option (a)

Covariance, A = $\frac{F}{V}\sum_{ijF}^{V}(x_i - \overline{x}_k)(y_i - \overline{y}_k)$

x	y	$x_i - \overline{x}_k$	$y_i - \overline{y}_k$
-1	1	$-1 - 0 =$	$1{-}12 = -1$
0	2	$0 - 0 = 0$	$1 - 2 = -1$
1	3	$1 - 0 = 1$	$3 - 2 = 1$

$\bar{x} = 0$ and $\bar{y} = \frac{l}{m} = 2$

thus A = $\frac{F}{m}\{(x_F - \bar{x})(y_F - \bar{y}) + x(\ _G - \bar{x})(y_G - \bar{y}) + x(\ _m - \bar{x})(y_m - \bar{y})\}$

$= \frac{F}{m}\{(-1)(-1) + 0(\ )(0) + 1(\ )(1)\}$

$= \frac{F}{m}\{1 + 1\}$

$= \frac{G}{m}$

Correlation Coefficient, $B = \frac{\sum(n_o 9 \overline{n}_p)(q_o 9 \overline{q}_p)}{\sqrt{\sum(n_o 9 \overline{n}_p)^T}\sqrt{\sum(q_o 9 \overline{q}_p)^T}}$

$x_i - \overline{x}_k$	$y_i - \overline{y}_k$
-1	-1
0	0
1	1

$$\sum(x_i - \bar{x})^G = (x_F - \bar{x})^G + (x_G - \bar{x})^G + (x_m - \bar{x})^G = (-1)^G + 0^G + 1^G = 2$$

$$\sum(y_i - \bar{y})^G = (y_F - \bar{y})^G + (y_G - \bar{y})^G + (y_m - \bar{y})^G = (-1)^G + 0^G + 1^G = 2$$

$$\sum(x_i - \overline{x}_k)(y_i - \overline{y}_k) = 2$$

QUANTA POINT

$$B = \frac{2}{\sqrt{2}\sqrt{2}} = 1$$

8. Correct option (b)

$x_{\mathrm{F}} = 15.8$ $x_{\mathrm{G}} = 15.4$ $x_{\mathrm{m}} = 15.6$ $x_{\mathrm{s}} = 16$

n = 4

$$\bar{x} = \frac{15.8 + 15.4 + 15.6 + 16}{4} = 15.7$$

$$\sigma = \sqrt{\frac{\sum(x_{\mathrm{i}} - \bar{x})^{\mathrm{G}}}{n}} = \sqrt{\frac{(x_{\mathrm{F}} - \bar{x})^{\mathrm{G}} + (x_{\mathrm{G}} - \bar{x})^{\mathrm{G}} + (x_{\mathrm{m}} - \bar{x})^{\mathrm{G}} + (x_{\mathrm{s}} - \bar{x})^{\mathrm{G}}}{n}}$$

$$= \sqrt{\frac{(\mathrm{FX.v9FX.w})^{\mathrm{T}}\mathrm{x}(\mathrm{FX.s9FX.w})^{\mathrm{T}}\mathrm{x}(\mathrm{FX.l9FX.w})^{\mathrm{T}}\mathrm{x}(\mathrm{Fl9FX.w})^{\mathrm{T}}}{\mathrm{s}}}$$

$$= \sqrt{\frac{(\mathrm{W.F})^{\mathrm{T}}\mathrm{x}(9\mathrm{W.m})^{\mathrm{T}}\mathrm{x}(9\mathrm{W.F})^{\mathrm{T}}\mathrm{x}(\mathrm{W.m})^{\mathrm{T}}}{\mathrm{s}}} = \sqrt{\frac{\mathrm{W.WFxW.WyxW.WFxW.Wy}}{\mathrm{s}}}$$

$$= \sqrt{\frac{\mathrm{W.G}}{\mathrm{s}}} = \sqrt{0.05}$$

variance (slosest value) = $\sigma^{\mathrm{G}} = \left(\sqrt{0.05}\right)^{\mathrm{G}} = 0.05$

9. Correct option (c)

n = 10, variance = 0.04, ∝ = 8

Standard deviation, σ = $\sqrt{\text{variance}} = \sqrt{0.04} = 0.20$

Coefficient of variance = $\frac{\}}{\sim} = \frac{\mathrm{W.G}}{\mathrm{v}} = 0.025$

Percentage coefficient of variance = 0.025×100% = 2.5%

10. Correct option (c)

four sets of measurements are 1.71×10^{-5} ,1.77×10^{-5} ,1.79×10^{-5} and 1.73×10^{-5}

therefore, average (mean) value = $\frac{(\mathrm{F.wFxF.wwxF.wyxF.wm})}{\mathrm{s}} \times 10^{9\mathrm{X}} = 1.76\times10^{9\mathrm{X}}$

QUANTA POINT

standard deviation, $\delta = \frac{\Sigma(\mathrm{n_o 9 \bar{n}})^{\mathrm{T}}}{\mathrm{V}}$

$= \sqrt{0.0010\times10^{9\mathrm{FW}}} = 0.0316\times10^{-5}$

which is in the range of $0.03\times10^{-5} - 0.039\times10^{-5}$

11. Correct option (d)

in a titration, the percentage uncertainties in the measured aliquot volume and the measured titre volume are ±x and ±y respectively.

The percentage error in concentration of aliquot is $(x^{\mathrm{G}} + y^{\mathrm{G}})^{\mathrm{F/G}}$

12. Correct option is (c)

Covariance shows the tendency in the linear relationship between the variables.

If $y = f(x) \propto x^n$(where n > 1), then $\mathrm{cov}(x, y) = +\mathrm{ve}$

If $y = f(x) \propto x^n$(where n < 0), then $\mathrm{cov}(x, y) = -\mathrm{ve}$

If $y = f(x) \propto x$, then $\mathrm{cov}(x, y) = 0$

For options (a), (b) and (d), $y \propto x^2 \Rightarrow \mathrm{cov}(x, y) = +\mathrm{ve}$

For option (c), $y \propto x$ $\mathrm{cov}(x, y) = 0$

13. Correct option (a)

$$\bar{x} = \left(\frac{3.2 + 5.2 + 7.2}{3}\right) ppb = 5.2ppb$$

$$s = \sqrt{\sum \frac{(x_i - \bar{x})^{\mathrm{G}}}{N-1}} = \sqrt{\frac{(3.2 - 5.2)^{\mathrm{G}} + (5.2 - 5.2\ )^{\mathrm{G}} + (7.2 - 5.2\ )^{\mathrm{G}}}{3-1}} ppb$$

$$= \sqrt{\frac{2^{\mathrm{G}} + 0^{\mathrm{G}} + 2^{\mathrm{G}}}{2}} ppb = \sqrt{\frac{8}{2}} ppb = 2 \qquad ppb$$

14. Correct option (b)

since, $f(x) = \frac{\mathrm{G}}{\sqrt{\mathrm{G\}^{T}„}}} e^{9(\mathrm{n9n\ \ †})^{\mathrm{T}}/\mathrm{G\}^{T}}}$ compare it with $f(x) = \frac{\mathrm{G}}{\sqrt{\mathrm{G‡^{T}„}}} e^{9(\mathrm{n9\hat{}\ \ })^{\mathrm{T}}/\mathrm{G‡^{T}}}$

variance = σ^{G}; on comparison, variance = a^{G}

QUANTA POINT

15. Correct option (c)

$$P(x) = e^{(-|2x-12|)} = e^{(-2|x-6|)} = f(x) = \begin{cases} e^{-2(x-6)}, & x > 6 \\ e^{2(x-6)}, & x < 6 \end{cases}$$

since the probability distribution is symmetric about x=6, therefore the average value of the physical observable ‘x’ will be equal to 6

QUANTA POINT